ANALYTICAL APPLICATIONS OF INORGANIC AND ORGANIC ION-EXCHANGERS

THESIS SUBMITTED
FOR THE DEGREE OF
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IN
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SUMMARY

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SUMMARY

The present work deals with an analytical approach to develop some methods of separation and determination of certain organic compounds and inorganic ions. The whole work is divided into five chapters. The first chapter deals with the general introduction covering a review on ion-exchangers in general and inorganic ion-exchangers in particular, based on the recent literature. The second chapter describes the use of inorganic ion-exchanger, zinc silicate as a new adsorbent for paper chromatographic separation of phenols. The third chapter describes the work on aluminium triethanolamine as a new inorganic anion exchanger while the fourth chapter deals with the development of a new chelating and anion exchanger, thorium triethanolamine. The fifth chapter deals with a sensitive and selective ion-exchange combined atomic absorption spectrophotometric determination of trace elements in rocks.

The second chapter describes the preparation of ion-exchange papers by precipitating zinc silicate within the pores of Whatmann No. 3 mm filter papers and the use of these papers for the chromatographic study of 27 phenols. Most of the sorbents used earlier lacked either in proper detection or adequate resolution of different phenols present in a mixture. In the present studies zinc silicate has been used as a potential sorbent for the phenols. The zones obtained

were compact with a clear detection. The solvent systems tried were aqueous solutions of different concentration of ammonia. Important separations were achieved when tried on the basis of some appreciable difference in R_f values of different phenols.

Chromatographic behaviour of these phenols have also been studied on the plain paper Whatmann No. 3 mm without any treatment of zinc silicate on them for comparison. R_f values on treated papers (known as R_{fT}) in most of the cases were lower than R_f values on untreated papers (known as R_{fU}). Lowering of R_{fT} is due to the ion-exchange behaviour of zinc silicate and this ion-exchange effect was measured in terms of R_i values where $R_i = R_{fU} - R_{fT}$. It is quite interesting to note that R_i remained constant for the different concentrations of NH_4OH, while R_i changed linearly with the number of OH groups present in the phenols.

The third chapter describes the studies on a new anion exchanger, aluminium triethanolamine which has been prepared by incorporated triethanolamine with the matrix of hydrous aluminium oxide. Out of the various inorganic ion-exchangers reported only a few which are the polyvalent metal hydroxides show anion exchange behaviour that too at low pH values. Such a limitation severely restricted their use for the separation of anions in the basic medium. In the present work the introduction of an amine group into the matrix of the metal

oxide has modified the behaviour. The studies revealed that the material, aluminium triethanolamine, showed anion exchange capacity both in acidic and basic media with a good selectivity towards chromate, sulphate, dichromate and thiosulphate ions.

The material was synthesized by blending 0.1M aluminium nitrate with 0.3M triethanolamine in the volume ratio of 1:1. The precipitate so obtained was filtered, washed and dried at 40°C. To characterize the material so formed the following studies were made: Composition, I.R.spectrum, potentiometric titrations, heat treatment and stability; while to study the anion exchange behaviour, anion exchange capacity, rate of exchange and K_d values were determined. Two molecules of triethanolamine are bound with one atom of aluminium and the presence of a C–O stretching vibration peak in I.R.spectrum indicates the linkage of metal with triethanolamine through oxygen atom. The potentiometric titration curve studies revealed the material to be a monofunctional anion exchanger. This material suffers some loss in its anion exchange capacity with increase in drying temperature above 60°C. The ion-exchange equilibrium was attained in 40 minutes which is relatively much shorter than the equilibrium time with other inorganic ion-exchangers. On the basis of large differences in K_d values successful separations of SCN^- from CrO_4^{--} and SO_4^{--}, I^- from SO_4^{--}, $S_2O_3^{--}$, $Cr_2O_7^{--}$ and CrO_4^{--}; Br^- from CrO_4^{--} and $S_2O_3^{--}$ were achieved.

The fourth chapter deals with the preparation and properties of a new inorganic chelating ion-exchanger, thorium triethanolamine which also works as an anion exchanger. It was prepared by mixing decimolar solutions of thorium nitrate and triethanolamine. The precipitate thus obtained was filtered, washed, dried at 40°C, cooled again and immersed into water to give small granules to be used for other studies. Anion exchange capacity was determined by column operation. The effect of concentration of the eluent or anion exchange capacity was also studied. The anion exchange capacity is because of a free charge on the nitrogen atom of the incorporated triethanolamine in this material. The chelating ion-exchange behaviour is studied in terms of sorption capacity towards various metal ions which were eluted by ethylenediamine tetra acetic acid. The material does not show any cation exchange behaviour indicating the possibility that there is no negatively charged ionogenic groups with the exchanger matrix, rather the sorption of metal ions took place due to the chelation between nitrogen of amine group and a metal ion. An interesting point in these studies is that the exchanger when treated with certain metal ion acquired a definite colour which can be conspicuously seen on the column.

This exchanger is quite stable in organic solvents and neutral aqueous solutions. Strong acidic media should be avoided, nevertheless, basic media can be used safely. The

exchanger has got another limitation of temperature and should be used below 100°C. The I.R. studies and chemical analysis may be helpful in tentative structure of the exchanger. Potentiometric titration curves indicated its monofunctional anion exchange behaviour.

Analytical potential of thorium triethanolamine was studied in terms of K_d values. A number of separations were tried on the basis of difference in K_d values and those practically achieved are listed. The anions were separated due to its anion exchange behaviour while the metal ions were separated due to its chelating anion exchange behaviour. Its fast exchange rate is an additional advantage over the other types of inorganic ion-exchangers.

The fifth chapter deals with a combined application of atomic absorption spectrometry with ion-exchange. The chemical analysis of naturally occurring materials viz. minerals, ores and rocks is an extremely complex operation. The study of the chemical composition of these materials is valuable for analytical chemists as well as geochemists and requires the use of accurate and sensitive methods. In the present work sensitive and selective method using ion-exchange precipitation has been developed for geochemical analysis where the various trace elements can be determined by prior separation over an anion exchange column. Applying principles of classical wet

analysis the quantitative determination of trace elements has been made in rock samples by converting an anion exchanger in the respective ionic forms to give the insoluble salts by the action of counter ion (an anion) of the resin and the metal ion in the solution. The metal ions are then eluted by suitable eluting reagents forming soluble salts. The different forms used were sulphide, hydroxyl, carbonate, chromate and sulphate. Different rock samples were examined for Mn(II), Zn(II), Ba(II), Ni(II), Cu(II) and Sr(II). The results have been compared with the standards.

Dedicated to my
Parents

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C E R T I F I C A T E

This is to certify that the work embodied in this thesis is original and is suitable for submission for the award of Ph.D. degree in Chemistry.

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Masood Alam.

(Masood Alam)

C O N T E N T S

LIST OF PUBLICATIONS

1. Zinc silicate as a new adsorbent for paper chromatographic separation of phenols.

   J.Liquid.Chromatogr. 5, 5, 1982.

2. Sensitive and selective ion-exchange combined A.A.S. determination of trace elements in rocks.

   Microchemical Journal (In Press).

3. Aluminium triethanolamine, a new inorganic ion-exchanger.

   Annali Di Chimica (Communicated).

4. Thorium triethanolamine as a new chelating and an anion exchanger.

   Chromatographia (Communicated).

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C H A P T E R - I

INTRODUCTION

The purpose of analytical researches is to develop new methods of analysis or to improve the existing ones. Therefore, analytical chemistry finds constant application in technology, industry, medicine, agriculture, geology and so many other fields of science. The importance of this branch can be recognized by the observation that at present no material is taken from a laboratory or released from a factory without its analytical data. Identification of the substances constitutes the branch qualitative analysis. Generally, the separation is the pre-treatment procedure for most of the determinations and sometimes for identifications. Thus all the three techniques together form the subject of chemical analysis. Chemical analysis is based upon classical and modern methods of analysis. The modern methods of analysis are divided into two broad groups viz. instrumental and non-instrumental. Instrumental techniques find their application in chemical analysis to a very high degree so much so that they have become backbone of experimental chemistry. The time is reduced, the sensitivity is increased. Some of the important techniques are spectrophotometry, polerography and voltametry. The non-instrumental techniques too are equally important in tackling various problems and are less expensive. The non-instrumental techniques are developed mainly for achieving seperations. The various methods that are employed for seperation are chromatography, electrophoresis, ion-exchange solvent extraction, ring oven techniques and

dialysis etc. Ion-exchange and chromatography are more versatile techniques in the field of separation science. Now-a-days the ion-exchange has come to be recognized as an extremely valuable technique. All over the world numerous plants are in operation for developing the separations of inorganic, organic and biochemical mixtures. Ion-exchange is a process in which an insoluble (or immiscible) material, when comes in contact with an electrolyte solution, takes up, stoichiometrically, ions of positive or negative charge and releases other ions of like charge from the exchanger phase into the solution phase. In laboratories ion-exchangers are used as an important tool for the solution of new problems facing our industrialists and scientists. The most important application of ion-exchange is the purification of water in an age when air and water pollution is leading to an alarming situation.

A description of ion-exchange process can be cited in the most ancient literature following a paragraph written in the holy Bible. Moses (1) wrote that the bitter water can be made drinkable by using pieces of wood. Aristotle (2) stated that sea water loses parts of a salt content when filtered through certain type of soil. The ion-exchange properties of wood cellulose in the first case and that of silicates in the second case might have served to improve the taste of water. For a long period no efforts were made to cite the ancient references.

The phenomenon of ion-exchange was rediscovered by Thompson (3) and Way (4) in 1850 by the name of "base exchange" in minerals present in soil. This was at the time when the studies were lacking in the existence of ions in solution. However, the phenomenon of "base exchange" was systematically studied to be reversible and to involve chemically equivalent quantities of the base taken up and of that released, nevertheless, it was recognized as an important phenomenon to soil fertility. It was established by Eichorn that zeolites were responsible for this exchange in soils (5). Aluminium silicate was first synthesized by Harms and Rumpler (6). According to Lemberg (7) and Wiegner (8) the materials responsible for this phenomenon were mainly clays, zeolites, glauconites and humic acids. These discoveries led to the use of the natural materials for water softening. Ambitious Gans adopted this technique to recover gold from sea water. But his ambition remained unfulfilled because the material of this type available at that time proved to be inadequate for the purpose. Gans (9) recognised the practical utility of the ion-exchange phenomenon for water softening using natural and synthetic zeolites and clays. The exhausted bed of the ion-exchanger was regenerated by passing a concentrated solution of sodium or potassium salts. Because of plausibility of regeneration these zeolites and clays could be used over and again. Limitations of zeolites and clays were soon realised, i.e. zeolites are decomposed by acids whereas clays are difficult to handle. To overcome these limitations a

search for stable ion-exchange material was started. In 1931 Kullgren (10) observed that sulphite cellulose works as an ion-exchanger for the determination of copper.

An interesting discovery began in 1935 when Adams and Holmes found that crushed phonograph records exhibit ion-exchange properties. This remarkable effect led the inventors to the synthesis of organic ion-exchange resins which had much better properties than any of the previous products (11). Various improvements were made in these resins, mainly after world war II by companies in U.S.A. and England. These resins are stable towards acids and easy to handle. The structure can be varied as desired, therefore, the difficulties observed with zeolites and clays were removed by the introduction of resins. Since then these organic ion-exchangers have been used both in laboratory and on industrial scale for separations, recoveries of metals, purification of water, concentration of electrolytes, reactions of precipitates and elucidating the mechanism of many reactions (12).

The applications of organic ion-exchange resins are also limited under certain conditions i.e. they are unstable in aqueous systems at high temperatures and in presence of the ionizing radiations. For these reasons there has been a revived interest in inorganic ion-exchangers in recent years, as they are unaffected by ionizing radiations and are less sensitive to higher temperatures. The structure of these inorganic ion-exchangers is stiff,

therefore, they are more selective and suitable for the separation of ions on the basis of their different sizes. For this reason they can also be used as ionic or molecular sieves. Being suitable towards ionizing radiations they can be used advantageously in reactor technology. In order to understand these applications and to improve upon them systematic fundamental studies are being pursued on these materials. This new interest in inorganic ion-exchanger may be said to begin in 1945. It was first shown by Boyd (13) that columns containing finely divided zirconium phosphate supported on silica gel could be used to separate uranium and plutonium from fission products by an ion-exchange process. In addition to zirconium phosphate many other similar substances may be prepared by combining oxides of group IV with the more acidic oxides of groups V and VI of the periodic Table. Such ion-exchangers are as follows:

TABLE I

SYNTHESIS AND ION-EXCHANGE PROPERTIES OF MULTIVALENT METAL SALTS

Sl. No.	MATERIAL	TYPE OF EXCHANGER	COMPOSITION	EMPERICAL FORMULA	I.E.C. (meq/g)	SELECTIVITY	REFERENCES
	(1) **Zirconium salts**						
1.	Zirconium phosphate	Amorphous	P/Zr=0.5-2.1	$Zr(OH)PO_4$	-	Cs^+, Rb^+, K^+, Na^+,	(14, 15, 16,
				$ZrO(HPO_4)$		Eu^{3+}, Sr^{2+}, Co^{2+},	17, 18, 19,
				$Zr_3(PO_4)_4$		Ni^{2+}, Zn^{2+}	20, 21, 22)
				$Zr(HPO_4)_2.H_2O$			
				$Zr(HPO_4)(H_2PO_4)OH$			
		Semi-crystalline	-	-	-	Li^+, K^+, H^+, Cs^+	
		Crystalline	-	$Zr(HPO_4)_2.H_2O$	-	Sr^{2+}, UO_2^{2+}, Ce^{3+}	(23, 24, 25)
2.	Zirconium pyrophosphate	Amorphous	P/Zr=2.0, 2.5-2.8	-	-	Cu^{2+}, Ni^{2+}, Ca^{2+},	(26, 27)
						Na^+, Fe^{2+}, Mg^{2+}	
3.	Zirconium hypophosphate	Amorphous	Zr/P=0.57	-	-	For multivalent metals	(28, 29, 30)
4.	Zirconium polyphosphate	Amorphous	-	-	-	For alkali metals (in NH_4^+ form)	(31, 32, 33)
						Fe^{3+}, Cu^{2+}, Ca^{2+}, Ba^{2+} (in H^+ form)	

TABLE I (Continued)

Sl. No.	MATERIAL	TYPE OF EXCHANGER	COMPOSITION	EMPERICAL FORMULA	I.E.C. (meq/g)	SELECTIVITY	REFERENCES
5.	Zirconium antimonate	Amorphous	-	$ZrO_2.Sb_2O_5.nH_2O$	-	Na^+,K^+,NH_4^+,Rb^+, Cs^+,Li^+	(34,35,36 37)
6.	Zirconium arsenate	Amorphous	As/Zr=1.55-1.96	$ZrO_2.0.8As_2O_5.nH_2O$	4.3	Cs^+,K^+,Na^+ (at pH 2.6) Na^+,K^+,Cs^+ (at pH 4.6)	(38,39)
		Crystalline	-	$Zr(HAsO_4)_2.H_2O$	5.1	Li^+,Na^+,K^+	(40)
7.	Zirconium molybdate	Amorphous	Zr/Mo=0.5-2.0	-	2.18	-	(41)
8.	Zirconium tungstate	Amorphous	Zr/W=1.0-0.44	-	-	Cs^+,Rb^+,K^+, Na^+,Li^+	(30,42,43, 44)
9.	Zirconium tellurate	Amorphous	-	$Zr(H_2TeO_6).4H_2O$	2.8	-	(45,46)
10.	Zirconium oxalate	Crystalline	-	$Zr(OH)C_2H_4H$	2.50	Na^+,Cs^+,Rb^+,K^+	(47)
11.	Zirconium silicate	Amorphous	Zr:Si=1:2	-	3.18	Th^{4+},Sm^{3+},Cs^{2+} As^+,Cr^{3+},Cu^{2+}	(48,49)

TABLE I (Continued)

Sl. No.	MATERIAL	TYPE OF EXCHANGER	COMPOSITION	EMPERICAL FORMULA	I.E.C. (meq/g)	SELECTIVITY	REFERENCES
12.	Zirconium ferrocyanide	Amorphous	Fe/Zr=0.63	-	0.96	Li^+,Na^+,NH_4^+,Zn^+, Zr^{4+}	(50,51)
13.	Zirconium oxide	Amorphous	-	$ZrO_2.4.7H_2O$	1.0	Ca^{2+},Ba^{2+}	(52,53)
			ZrO_2/H_2O=0.048	$ZrO_2.2.2H_2O$	-	Cu^{2+},Zn^{2+},Cd^{2+}, Co^{2+},Mn^{2+},Ca^{2+}	(54,55,56)
14.	Zirconium selenite	Amorphous	SeO_3^{2-}/ZrO_2=0.8	-	0.48	Ag^+,Cu^{2+},Am^{3+}	(57)
15.	Zirconium vanadate	Amorphous	-	-	2	-	(58)
(11)	Thorium salts						
16.	Thorium phosphate	Crystalline	Th/PO_4=0.5	$Th(HPO_4)_2.2H_2O$	0.77	Ca^{2+},Ba^{2+},Sr^{2+}	(59)
		Fibrous	-	$ThO_2.P_2O_5.2H_2O$	3.8	-	(60)
17.	Thorium arsenate	Crystalline	As/Th=1.53-1.96	$Th(HAsO_4)_2.H_2O$	0.20	Li^+	(61,62)
18.	Thorium molybdate	Amorphous	Th/Mo=0.50	-	0.75	Fe^{3+},Zr^{4+},Pb^{2+}	(63)
19.	Thorium tungstate	Amorphous	Th/W=2.0	$Th(OH)_2(HWO_4)_2.nH_2O$	0.46	Cs^+,K^+,Na^+,Ba^{2+}, Hg^{2+},VO^{2+},La^{3+}	(64,65)

TABLE I (Continued)

Sl. No.	MATERIAL	TYPE OF EXCHANGER	COMPOSITION	EMPERICAL FORMULA	I.E.C. (meq/g)	SELECTIVITY	REFERENCES
20.	Thorium antimonate	Amorphous	Sb/Th=3.65	-	0.32	Pb^{2+},Cu^{2+}	(66)
21.	Thorium oxide	Amorphous	-	$Th(OH)_n.mH_2O$	2.0	Ca^{2+},Sr^{2+},Cs^{+}, Na^{+},Rb^{+}	(67,68,69)
	(iii) Titanium salts						
22.	Titanium phosphate	Amorphous	P/Ti=0.6-2.0	$TiO_2.0.65P_2O_5.nH_2O$			(70,71,72, 73,74,75, 76,77)
				$(TiO)_{0.535}(H_2PO_4)_{0.369}(OH)_{1.77}.1.1H_2O$			
				$TiH_2(PO_4)_2.4H_2O$	7.5	Cs^{+}	(78)
				$Ti(PO_4)_4$	7.15	-	
		Crystalline	P/Ti=0.6-2.0	$Ti(HPO_4)_2.H_2O$	7.0	Zr^{4+},Nb^{5+},Na^{+}	
				$Ti(HPO_4)_2.2H_2O$	7.2	Sr^{2+}	
23.	Titanium arsenate	Amorphous	-	$Ti(HAsO_4)_2.2.5H_2O$	1.0	Pb^{2+},Cu^{2+},Ba^{2+}	(79,80,81, 82,83)
				$TiO_2.0.5As_2O_5.nH_2O$		Sr^{2+},Zn^{2+},Cd^{2+}	
		Crystalline		$Ti(HAsO_4)_2.H_2O$	5.80		

TABLE I (Continued)

Sl. No.	MATERIAL	TYPE OF EXCHANGER	COMPOSITION	EMPERICAL FORMULA	I.E.C. (meq/g)	SELECTIVITY	REFERENCES
24.	Titanium antimonate	Amorphous	Sb/Ti=1-1.36	-	0.70	Rare earth metals Mg^{2+}, VO^{2+}, Zn^{2+}	(84,85,86)
25.	Titanium molybdate	Amorphous	Mo/Ti=0.5-2.0	-	0.8-1.60	Na^{+}, K^{+}, Ba^{2+}, Pb^{2+}, Tl^{+}	(87,88,75)
26.	Titanium tungstate	Amorphous	Ti:W=3:4	-	0.4-0.76	Ca^{2+}, Zr^{4+}, Ce^{+}, Ga^{3+}	(88,89,90, 91,92,93)
27.	Titanium selenite	Amorphous	Ti/Se=1.39	-	0.78	Cd^{2+}	(94)
28.	Titanium vanadate	Amorphous	V/Ti=4.0	$Ti_5(V_5O_9 \cdot 1.5H_2O)_4 \cdot 15H_2O$	0.68	Sr^{2+}	(95,96)
29.	Titanium tellurate	Amorphous	Te/Ti=2.06	-	-	-	(97)
30.	Titanium ferrocyanide	Amorphous	$Fe(CN)_6^{4-}$/Ti=2.0	-	1.40	Cs^{+}	(98)
31.	Titanium oxide	Amorphous	-	$TiO(OH)_2 \cdot nH_2O$	2.0	Na^{+}, Cs^{+}, Rb^{+}, Ce^{2+}	(68,69,99)
32.	Titanium silicate	Amorphous	Ti/Si=1	-	3.62	Li^{+}, Na^{+}, Pb^{2+}, K^{+}, Cr^{3+}	(100)

TABLE I (Continued)

Sl. No.	MATERIAL	TYPE OF EXCHANGER	COMPOSITION	EMPERICAL FORMULA	I.E.C. (meq/g)	SELECTIVITY	REFERENCES
	(iv) Cerium(IV) salts						
35.	Cerium phosphate	Amorphous	P/Ce=1.03-1.95	$Ce_3(OH)_8(H_2PO_4).nH_2O$	2.90	Ce^+,Rb^+,K^+,Na^+,Li^+	(101,102,10
		Micro-crystalline	P/Ce=1.5	$Ce-O-Ce(HPO_4)_3.H_2O$	-	Na^+,Ag^+,Ca^+	104,105,10
		Crystalline	-	$Ce(HPO_4)_2.H_2O$	5.30	-	110,111)
36.	Cerium arsenate	Crystalline	As/Ce=2.0	$Ce(HAsO_4)_2.2H_2O$	4.30	Na^+,K^+,Li^+,Ca^+	(112,113)
37.	Cerium molybdate	Amorphous	Mo/Ce=2.33-8.29	-	0.96	Pb^{2+}	(114,115)
38.	Cerium antimonate	Amorphous	Sb/Ce=0.30-0.33	-	1.25	Hg^{2+},Te^+,Cu^{2+}	(116)
39.	Cerium tungstate	Amorphous	Ce/WO_4^{2-}=0.49	-	0.89	Hg^{2+},Al^{3+}	(117)
40.	Cerium oxide	Amorphous	$H_2O:CeO_2$=3.00	-	0.99	Cu^{2+}	(118)

TABLE I (Continued)

Sl. No.	MATERIAL	TYPE OF EXCHANGER	COMPOSITION	EMPERICAL FORMULA	I.E.C. (meq/g)	SELECTIVITY	REFERENCES
	(v) Tin(IV) salts						
39.	Stannic phosphate	Amorphous	P/Sn=1.25-1.50	$SnO_2.0.62P_2O_5.nH_2O$	1.30-1.44	Cs^+,Rb^+,K^+,Na^+, Li^+,Cu^{2+},Zn^{2+}, Ni^{2+},Ce^{2+}	(119,120,121, 122,123,124, 125,126)
		Crystalline	-	$SnO_2.P_2O_5.2H_2O$	4.7	Zr^{4+}	
40.	Stannic arsenate	Amorphous	Sn/As=1.84	-	0.79-0.94	Al^{3+},Ga^{3+},In^{3+}, Fe^{3+},Pb^{2+}	(127,128,129, 129,130,131)
		Crystalline	-	$SnO_2.As_2O_5.2H_2O$	3.8	Li^+,K^+,Na^+	
41.	Stannic molybdate	Amorphous	Sn/Mo=1.0	-	1.0	Pb^{2+}	(132)
42.	Stannic tungstate	Semi-transparent	Sn/W=1:3	-	0.58	Co^{2+},Ba^{2+},Ni^{2+}, Pb^{2+},Mn^{2+},Ca^{2+}, Sr^{2+}	(133)
43.	Stannic antimonate	Amorphous	Sb/Sn=1.0	$SnO_2.Sb_2O_5.nH_2O$	0.75	Cu^{2+},Ni^{2+},Co^{2+}	(134,135)
44.	Stannic selenite	Amorphous	Sn/Se=1.33	$(SnO_4)(OH)_2(SeO_3).6H_2O$	0.75	Li^+,Na^+,K^+	(136,137)

TABLE I (Continued)

Sl. No.	MATERIAL	TYPE OF EXCHANGER	COMPOSITION	EMPERICAL FORMULA	I.E.C. (meq/g)	SELECTIVITY	REFERENCES
45.	Stannic ferrocyanide	Amorphous	Sn/Fe=3.0	$(SnO)_3.(OH)_3.H_4Fe(CN)_6.3H_2O$	2.02	K^+, Ba^{2+}, Na^+	(138,139)
46.	Stannic vanadate	Amorphous	Sn/V=1.0	$Sn(OH)_3V_3O_9.4H_2O$ n	2.85	K^+, Na^+, Li^+	(140)
47.	Stannic oxide	Amorphous	-	-	1.98	$Cu^{2+}, Zn^{2+}, Co^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}$	(141,142,14 144)
48.	Stannic silicate	Amorphous	Sn/Si=4.0	-	-	$Cr^{3+}, Pb^{2+}, Cu^{2+}$	(145)
	(vi) Chromium(III) salts						
49.	Chromium phosphate	Amorphous (Polyfunctional)	P/Cr=0.6-1.0	$Cr_2O_2HPO_4$	5.9	$Na^+, K^+, Rb^+, Cs^+, Li^+$	(146,147,14 149,150,15
				$Cr_2O(HPO_4)_2$		$Cs^{2+}, Sr^{2+}, Ba^{2+}$	
50.	Chromium tripolyphosphate	Glass solid	Cr/P=1.2-0.48	$Cr_5(P_3O_{10})_3.nH_2O$	-	$Zr^{4+}, Cs^+, Rb^+, K^+, Na^+$	(152,153,15
51.	Chromium arsenate	Amorphous	As/Cr=1.98	$Cr_2O_3(H_3AsO_4)_4.3H_2O$	0.63	Zr^{4+}, Hf^{4+}	(155)
52.	Chromium antimonate	Amorphous	Sb/Cr=2.95	$Cr_2O_3.3Sb_2O_5.22H_2O$	0.42	Pb^{2+}, Ce^{2+}	(155,156)

TABLE I (Continued)

SL. NO.	MATERIAL	TYPE OF EXCHANGER	COMPOSITION	EMPERICAL FORMULA	I.E.C. (meq/g)	SELECTIVITY	REFERENCES
53.	Chromium molybdate	Amorphous	Mo/Cr=1.90	$Cr_2O_3(H_2.MoO_4)_4.8H_2O$	0.34	Pb^{2+},Ga^{3+}	(155)
54.	Chromium tungstate	Amorphous	W/Cr=1.92	$Cr_2O_3(H_2WO_4)$.$11H_2O$	0.02	Th^{4+},Hf^{4+}	(155)
55.	Chromium tellurate	Amorphous	Te:Cr=0.2	-	-	-	(97)
56.	Chromium ferrocyanide	Amorphous	Cr/Fe=0.327	$K_6Cr_2Fe(CN)_3$ $16H_2O$	2.65	Li^+,Na^+,K^+,Ca^{2+}, Ba^{2+}	(157)
	(vii) Iron(III) salts						
57.	Ferric phosphate	Amorphous	P/Fe=2.0	$FeH(HPO_4)_2.nH_2O$	0.77	Pb^{2+},Eu^{3+},Ce^{3+}	(158,159)
58.	Ferric pyrophosphate	Amorphous	-	$Fe_4(P_2O_7)_3$	-	In^{3+}	(160)
59.	Ferric arsenate	Amorphous	As/Fe=1.35	-	0.80	K^+,Na^+,Li^+	(161)
60.	Ferric antimonate	Amorphous	Sb/Fe=2.4	-	0.80	Cs^{2+}	(162,163)
61.	Ferric tungstate	Amorphous	Fe/W=1.0	-	0.84	Ce^{4+}	(164)

TABLE I (Continued)

Sl. No.	MATERIAL	TYPE OF EXCHANGER	COMPOSITION	EMPIRICAL FORMULA	I.E.C. (meq/g)	SELECTIVITY	REFERENCES
62.	Ferric ferrocyanide	Amorphous	-	-	3.60	Cs^+	(165)
63.	Ferric silicate	Amorphous	-	-	0.20-1.60	Cr^{3+}, Cd^{2+}, Al^{3+}, Zn^{2+}	(166)
	(viii) Aluminium(III) salts						
64.	Aluminium triphosphate	Amorphous	Al/P=0.5-0.66	-	2.50	-	(158)
65.	Aluminium vanadate	Amorphous	-	$(Al_2O_3)_4(V_2O_5)_n$	-	-	(167)
66.	Aluminium antimonate	Amorphous	Al/Sb=4.2	-	1.14	Ag^+, UO_2^{2+}, Ba^{2+}, Tl^{4+}	(168,169)
67.	Aluminium oxide	Crystalline	-	-	-	-	(144,170)
	(ix) Tantalum(V) salts						
68.	Tantalum phosphate	Amorphous	-	-	-	-	(171)
69.	Tantalum arsenate	Amorphous	Ta/As=2.50	-	1.09	Na^+, K^+, Ba^{2+}	(172)
70.	Tantalum antimonate	Amorphous	Ta/Sb=1.30	-	0.00	Na^+, K^+, NH_4^+, VO^{+2}	(173)

TABLE I (Continued)

Sl. No.	MATERIAL	TYPE OF EXCHANGER	COMPOSITION	EMPERICAL FORMULA	I.E.C. (meq/g)	SELECTIVITY	REFERENCE
71.	Tantalum pentoxide	Amorphous	-	-	-	-	(174,175)
72.	Tantalum selenite	Amorphous	Ta:Se=1:1.5	-	1.19	Fe^{3+},Mn^{2+}	(176)
73.	Tantalum tungstate	Amorphous	-	-	0.84	K^{+}	(177)
	(z) Niobium(V) salts						
74.	Niobium phosphate	Amorphous	-	-	-	-	(178,179)
75.	Niobium arsenate	Amorphous	Nb/As=1.96	-	1.06	Mg^{2+},Cd^{2+},Mn^{2+},Al^{3+}	(180)
76.	Niobium antimonate	Semi-crystalline	Nb/Sb=1.40	-	1.10	Mg^{2+}	(181)
		Crystalline	-	$Nb_2.Sb_5O_{10}(OH)_5.2H_2O$	0.90	NH_4^{+}	(182)
77.	Niobium vanadate	Amorphous	-	-	-	Ce^{3+},Eu^{3+}	(183)
78.	Niobium pentoxide	Amorphous	-	-	-	-	(184,185)

TABLE I (Continued)

Sl. No.	MATERIAL	TYPE OF EXCHANGER	COMPOSITION	EMPERICAL FORMULA	I.E.C. (meq/g)	SELECTIVITY	REFERENCES
	(xi) Bismuth(III) salts						
79.	Bismuth nitrate	Amorphous (In basic medium)	-	-	-	-	(186)
.	Bismuth tungstate	Amorphous	Bi/W=0.5	-	0.50	Pb^{2+}	(187)
81.	Bismuth tellurate	Amorphous	Te/Bi=0.70	$Bi_4(H_2TeO_6)_3.mH_2O$	3.2	-	(188)
82.	Bismuth silicate	Amorphous	-	-	3.3	-	(189)
	(xii) Lead(II) salts						
83.	Lead phosphate	Crystalline	-	$Pb(HPO_4)_2.H_2O$	4.79	-	(123)
84.	Lead tungstate	Amorphous	Pb:W=1:2.5	-	1.0	Cu^{2+}	(190)
85.	Lead ferrocyanide	Amorphous	-	$Pb_2Fe(CN)_6$	-	Cs^{+},Co^{2+}	(191)
	(xiii) Other acidic salts						
86.	Lanthanum tellurate	Amorphous	La/Te=0.66	$La_2(TeO_4)_3$	1.61	-	(192)

TABLE I (Continued)

Sl. No.	MATERIAL	TYPE OF EXCHANGER	COMPOSITION	EMPERICAL FORMULA	I.E.C. (meq/g)	SELECTIVITY	REFERENCES
87.	Lanthanum oxalate	Amorphous	-	-	-	-	(193)
88.	Cobalt ferrocyanide	Amorphous	-	-	-	Ag^{+}	(194,195,19 196
89.	Cobalt antimonate	Amorphous	Co/Sb=1.3:1	-	0.89	Bi^{3+}	(197)
90.	Nickel antimonate	Amorphous	Ni/Sb=1.3:1	-	0.89	Bi^{3+}	(197)
91.	Nickel ferrocyanide	Amorphous	-	-	-	Cs^{+},Rb^{2+}	(198,199,20
92.	Tungsten ferrocyanide	Amorphous	W/Fe=1.32	-	1.02	-	(201)
93.	Molybdate ferrocyanide	Semi-crystalline	Fe/Mo=2.3	$H_4Fe(CN)_6.4MoO_3(H_2O)_n$	1.20	Cs^{+}	(202,203)
94.	Antimonic acid	Amorphous crystalline	-	$Sb_2O_5.4H_2O$	1.28	K^{+},Li^{+},Na^{+},Sr^{2+}, Ta^{5+}	(204,205,20 207,208)
95.	Uranyl hydrogen phosphate	-	-	$UO_2HPO_4.4H_2O$	-	Cs^{+},Rb^{+},K^{+}	(209)
96.	Vanadium ferrocyanide	Amorphous	V/Fe=0.93	-	2.36	Cs^{+},Rb^{+}	(210)

TABLE I (Continued)

Sl. No.	MATERIAL	TYPE OF EXCHANGER	COMPOSITION	EMPERICAL FORMULA	I.E.C. (meq/g)	SELECTIVITY	REFERENCES
97.	Stannous ferrocyanide	Amorphous	Sn/Fe=1.0	$SnO.H_4Fe(CN)_6.2.5H_2O$ n	2.03	Cu^{2+},Ni^{2+},Mn^{2+}	(211)
98.	Zinc ferrocyanide	Amorphous	Zn/Fe=1.98	$Zn_2Fe(CN)_6$	6.10	Cs^{+},Ag^{+}	(212,213)
99.	Zinc silicate	Amorphous	Zn/Si=1:1.25	-	2.0	Mg^{2+},Sr^{2+},Ba^{2+},H^{+}	(214,215,2[24]
100.	Zinc phosphate	Amorphous	-	-	-	-	(217)
101.	Lanthanum tungstate	-	-	-	-	-	(218)
102.	Copper phosphate	Amorphous	-	-	-	-	(219)
103.	Copper ferrocyanide	Amorphous	-	-	-	-	(220,221)
104.	Hafnium phosphate	Crystalline	-	$Hf(HPO_4)_2.H_2O$	4.17	-	(222)
105.	Germanium(IV) phosphate	Crystalline	-	$Ge(HPO_4)_2.H_2O$	7.08	-	(223)

TABLE I (Continued)

Sl. No.	MATERIAL	TYPE OF EXCHANGER	COMPOSITION	EMPERICAL FORMULA	I.E.C. (meq/g)	SELECTIVITY	REFERENCES
	(xiv) Double salts						
106.	Zirconium phosphosilicate	Amorphous	-	-	2.2	Pu^{4+},Cs^{+}	(224,225, 226)
107.	Zirconium molybdophosphate	-	-	$ZrH_2Mo_6O_{21}.xH_2O$	1.6	-	(227)
108.	Zirconium molybdovanadate	-	Zr :V:Mo = 1.68:1:0.068, 5.33:1:0.28, 6.15:1:0.815.	-	-	Li^{+},Na^{+}	(228)
109.	Zirconium titaniumphosphate	Crystalline	Zr/Ti=3.25	$Zr_xTi_{1-x}(HPO_4)_2.H_2O$ x = 0.77	6.87	-	(229)
110.	Zirconium ceriumphosphate	-	-	-	-	-	(230)
111.	Titanium phosphosilicate	Amorphous	-	-	-	Zr^{4+},Nb^{3+},Cs^{+}	(231)
112.	Titanium molybdophosphate	-	-	-	-	-	(227)
113.	Titanium tungstophosphate	-	-	-	-	Th^{4+}	(232)

TABLE I (Continued)

Sl. No.	Material	Type of Exchanger	Composition	Empirical Formula	I.E.C. (meq/g)	Selectivity	References
114.	Titanium tungstoarsenate	-	Ti:W:As = 3.22:1:1.38	-	1.26	-	(233)
115.	Stannic arsenophosphate	Amorphous	Sn:As:P = 1.7:1 :1	$(SnO_2)_5.(H_5AsO_4)_3.(H_5PO_4)_3\ .mH_2O$		Tb^{4+},Zr^{4+},K^+	(234,235)
116.	Stannic vanadophosphate	Crystalline	-	-	1.98	Ba^{2+},Cu^{2+}	(236)
117.	Stannic vanadoarsenate	Amorphous	Sn:V :As = 1.9:1.14:1.1	-	1.20	Ba^{2+}	(237)
118.	Stannic molybdoarsenate	Amorphous	Sn:Mo:As = 2: 1 : 1	-	1.40	-	(238)
119.	Stannic tungstoarsenate	Amorphous	Sn:W:As = 12:5:2	-	1.06	Ba^{2+},Cu^{2+}	(239)
120.	Stannic vanado tungstate	-	-	-	-	-	(240)
121.	Chromium arsenophosphate	Amorphous	Cr:As:P = 2: 1 :1	$Cr_2O_3.H_3AsO_4.H_3PO_4\ .mH_2O$	0.74	K^+	(234,235)
122.	Lead strontiumphosphate	-	-	-	-	-	(241)
123.	Pyridium tungstoarsenate	-	-	$(C_5H_5NH)_3H_{18}AsO_4$	-	Ag^+,Cs^+	(242)
124.	Pyridium tungstoarsenate	-	-	-	-	UO_2^+,Cs^+,Tl^+	(243)

A new class of ion-exchange resins was developed by Gregor in 1952 by substituting a chelate group in a highly crosslinked hydrocarbon matrix. Since then many such substances known as chelating ion-exchanger have been described in the literature. In these types of exchangers the use of chemical reactions can also be considered to play an important role. The chelating ion-exchange materials behave alike true ion-exchangers and the functional group is a chelating group which is fixed within the matrix. Formation of a complex with a metal ion is an example of a coordination compound in which the donor of lone pair of electrones is the complexing agent and the central metal ion forms a coordinate-covalent bond with it. The formation of the complex depends upon the stability constant of the chelate formed.

A large number of processes for the preparation of chelating ion-exchangers have been cited in the literature in the recent past. They are based mainly on condensation, polymerization or addition polymerization and introduction of chelating function either during polymerization or attaching after polymerization.

Varied physical forms may thus be obtained with such a wide range of preparations. Further the nature of chemical additions is based on the introduction of wide range of materials. Chelating exchangers thus have the desirable properties of high capacity, high selectivity, kinetics and high mechanical strength.

In addition to the materials mentioned so far a number of other types of exchangers have been developed. In particular, electron exchangers, redox exchangers and chelate ion-exchangers have found the highest interest of all such materials. The electron exchangers may be considered as solid oxidation and reducing agents. They contain the species forming a redox couple and after having oxidised (or reduced) a substrate the electron exchangers can be regenerated by a suitable oxidizing or reducing agent. The reactivity of electron exchangers is due to built-in redox components. The most important advantage of electron exchangers over dissolved oxidising or reducing agents is their insolubility and hence an electron exchanger can be easily separated from the solution containing a substrate being oxidised or reduced. The solution is free from the contamination of any redox agent or its products. Only electrons and protons are transferred between the resin and the solution. Therefore, the only possible change in the solution, except for the redox reaction of the substrate, is a change in pH. Another advantage of electron exchangers is that they can be readily regenerated (oxidised or reduced) after use.

The electron exchangers are characterised by their redox capacity, redox potential and reaction rate. The redox capacity is the amount (in equivalents) of a substrate being oxidised or reduced by a specified amount of the exchanger. The reaction rate indicates the time required for redox process under a given set of conditions.

Vernon (244) has summerized the nature of such compounds recently. Polycondensation has been applied by Meyer (245,246) for the preparation of chelating exchangers containing glyoxal bis-2-hydroxyanil groups and he successfully recovered copper and uranium from sea water by the use of these materials. He also produced a sulphur analogue resin which is selective to silver, gold, mercury and which has also been used for the recovery of gold from sea water, a problem first taken by Gans (9). The chelating agent may also be placed in the mobile phase, using a non ionic reverse phase support, which essentially becomes a cation exchanger (247).

Formation of a complex with a metal ion is an example of a coordination compound in which the donor of lone pair of electrones is the complexing agent and the central metal ion forms a coordinate-covalent bond with it. The formation of the complex depends upon the stability constant of the chelate formed. The interest in this field has been developed recently and such exchangers are reported in Table II.

TABLE II

SOME OF THE CHELATING ION-EXCHANGE RESINS

SL. NO.	TYPE OF CHELATING RESIN	SORPTION CAPACITY, (m.moles/g)	SELECTIVITY	REFERENCE
1.	Oxime and diethylamine resin	2.00	Cu(II)	(248)
2.	8-hydroxyquinoline and 8-hydroxyquinaldine resin	-	Cu(II) and Zn(II)	(249)
3.	O-hydroxyoxime resin	-	Mo(VI) and Cu(II)	(250)
4.	Thioglycolate resin	-	Ag(I), Bi(III), Sn(IV), Sb(III), Hg(II) from 0.1N acid; Cd(II), Pb(II), U(VI) from pH 3.5	(251)
5.	Amino acid type resin	-	U(VI), Cu(II), Ni(II) and Fe(III)	(252)
6.	Phosphate type resin	-	U(VI) and Th(IV)	(252)
7.	N-Acylphenyl-hydroxylamines	0.45	-	(253)

The studies of inorganic based chelate exchangers are meagre. Therefore, the synthesis and use of such exchangers in chemical analysis may be of importance. A new approach has been tried to introduce the complexing agents with the matrix of the exchanger. On this basis aluminium triethanolamine and thorium triethanolamine have been synthesized. Thorium triethanolamine has been found to behave as a good chelating exchanger.

For a complete description of a material as an ion-exchanger the following properties must be studied;

1. The ion-exchange capacity,
2. The resistance towards acids and bases,
3. Composition,
4. Potentiometric titrations,
5. Distribution of counter ions between solution and exchanger phases,
6. Kinetics,
7. Thermodynamics, and
8. Analytical applications.

Ion-exchange capacity is one of the most fundamental quantities for characterization of any ion-exchange material. For a strong ion-exchanger, the capacity can readily be determined by direct titration. Various types of capacities can be expressed in different manners. The equilibrium ion-exchange capacity for a

strong ion-exchanger can be determined by direct titration of strong cation exchanger (in H^+ form) with a strong base. Majority of the synthetic inorganic ion-exchangers behave as a weak ion-exchanger and therefore, the direct titration is not reliable. In this case ion-exchange capacity is determined by replacement of hydrogen ions from the exchanger phase by the counter ions of a neutral salt solution and then determination of the equilibrium ion-exchange capacity is done by pH-titrations. Maximum ion-exchange capacity equal to the number of ionogenic groups per specified amount of ion-exchanger may directly be determined by simple column operation passing the electrolytic solution over the ion-exchange material (in H^+ form) and titrating the liberated acid in the effluent by a standard base solution. Although the pure ion-exchange capacity of a solid ion-exchanger can be determined in several ways, a gravimetric method (254) offers for many ion-exchangers the advantage of relatively high accuracy and very simple equipment requirements for only one difference weighing without any analytical chemical determination of ion. Breakthrough capacity (255) i.e., the useful capacity for utilising the column operations, is of importance when the rate of exchange is slow. This rate may be so slow that the total capacity may not be utilised in an actual operation. The operation is discontinued at breakthrough before reaching the complete equilibrium. This capacity which is utilised until breakthrough occurs is known as breakthrough capacity or dynamic

capacity. It depends upon operating conditions and is lower than the equilibrium ion-exchange capacity.

The ion-exchange material must be studied for chemical stability in acidic and basic media to check its limitations.

The distribution of an ion between the exchanger and solution phases is a measurement of selectivity. Often, the ion-exchanger takes up certain ions in preference to the other present counter ions. This selectivity may depend, mainly upon: (i) Donnan potential, (ii) sieve action, and (iii) complex formation. The selectivity is an important factor to study the separations. On the basis of distribution coefficients it is possible to predict the separation of one ion from the other.

The inorganic ion-exchangers have found numerous important analytical applications as categorized below:

(i) Purification of substances on a large scale,

(ii) Separation of one ion from the other on a small ion-exchanger column,

(iii) Ion-exchange paper chromatographic separations,

(iv) Electrophoresis,

(v) Ion-exchanger for gas chromatography,

(vi) Solid state separations,

(vii) Specific spot tests,

(viii) Use of ion-exchanger beads to locate the end point in titration, and

(ix) Use of ion selective electrodes.

Purification on a large scale can be made by passing the sample solution through the ion-exchanger beds which take up certain materials in preference of others. The exchanger bed can be regenerated into suitable form by conventional methods (256). The technique can also be utilised to recover traces of elements from the dilute solutions. The elements present in ionic form are exchanged by equivalent amount of the counter ion present in the exchanger. The elements can be eluted from the exchanger by suitable electrolytic reagent. Ion-exchange is, with very few exceptions, a reversible process. The metallic ions are exchanged stoichiometrically with hydrogen ions in exchanger phase and the metal ions can be determined indirectly by the application of exchange reactions:

$$nRH^{+} + M^{n+} \rightleftharpoons MR_n + nH^{+}$$

where R represents the structural unit of the ion-exchanger, and H^{+} and M^{n+} are the cations taking part in the ion-exchange. A similar method can be adopted for the replacement of anions by hydroxyl ions stoichiometrically.

Ion-exchange has resolved the most difficult problem in chemical analysis i.e. separation of typical components having similar enough properties. Column chromatography is valuable, since the substances seperated are collected quantitatively.

Since the crystalline ion-exchangers have cavities of definite size, they also possess ion sieve properties. The counter ions having larger radii than the holes in the cavity cannot penetrate and therefore, they can be separated from those smaller ions which can easily enter into the cavity. These separations were first achieved by Clearfield on zirconium phosphate crystals (257) and are summarized below:

Zirconium phosphate and anhydrous metal salt were heated in a platinum dish. The exchange reaction taking place is represented by the following equation:

$$Zr(HPO_4)_2.H_2O + 2/X\ MCl_X \rightleftharpoons Zr(M)_{2/X}\ (PO_4)_2 + 2HCl + H_2O$$

When zinc chloride or hafnium chloride were exchanged a new phase was obtained which persisted to about 2/3 of total capacity of the exchanger. These wide ranges of metal content forming the same structure indicate that solid solutions of cation within crystal lattice are forming. The fact that a variety of cation type gives the same phases (almost identical interplanar spacing but different intensities) indicates that the crystal lattice remains rigid with the cations occupying similar exchange sites. This is unlike the behaviour of zirconium phosphate exchanging ions in aqueous electrolyte solution where the lattice expands by the movement of the α-zirconium phosphate layers to accommodate hydrated cations. The elution of cations with dilute acid solutions

proved the phenomenon as ion-exchange, the cations could also be removed by contacting the exchange phases with gaseous hydrogen chloride.

Some ion-exchange separations were also achieved. A solution containing equal parts of lithium chloride and caesium chloride was evaporated to dryness and the dry salt mixture was ground together with ∝-zirconium phosphate. On heating the mixture at 125°C lithium exchanged leaving caesium because the cavities are large enough to permit a cation of about 2-5° A. Thus Cs^+ should be excluded as was observed experimentally.

However, very few literature is available on ion-exchange in molten salt. Alberti and Allulli (258) treated ion-exchange on amorphous zirconium phosphate in molten nitrates. They found that lithium ion is greatly preferred over potassium ions by the exchanger.

Alberti also studied the specific conductance of amorphous zirconium phosphate in Li^+, Na^+, K^+ and Cs^+ forms over the range 2-40% conversions (259). The specific conductance of Li^+ and Cs^+ forms was found to decrease with percent conversion while that of the Na^+ and K^+ forms first increases and then decreases as conversion proceeds. A tentative model was proposed to explain the observed phenomenon.

The most difficult operation in chemical analysis is the separation of components into the forms used for the easy determi-

mations. Several methods have been developed for this purpose. Chromatography and ion-exchange have revolutionary effects on this analysis. Chromatography reduces the time duration to a great extent. This technique is extremely valuable, since compounds which are similar enough to defy separation by any other method are often resolved by quite simple chromatographic procedures. Column chromatography is valuable, since the substances separated are collected quantitatively. An important development which enables the use of paper separations as a preparative separation technique and which utilizes to advantage the combined effects of paper chromatography and ion-exchange is the chromatography on papers impregnated with ion-exchangers. The equipment necessary is very simple. These ion-exchange papers are easily prepared by treating them with precipitating electrolytic solutions one after the other (260). The separations achieved on these papers are rapid, selective and clean, and are, therefore, extensively used for analytically and biochemically important separations. Some important separations of organic substances on these papers are listed in Table III.

Although other chromatographic techniques have been introduced in recent years but paper chromatography still remains the most important method for phenolic compounds.

The phenolic compounds may be classified as simple

phenolics and flavonoids. Simple phenolics include phenols, such as chatechol and resorcinol; phenolic acids such as cinnamic acids. The flavonoides comprise the widely occurring water soluble plant pigments, the anthocyanins and flavones, and a number of related substances. The discussion will be confined to simple phenolics only. Chromatography of phenols on ion-exchanger loaded papers gives high selectivity and is used here.

TABLE III

SEPARATION OF ORGANIC SUBSTANCES ACHIEVED ON PAPERS IMPREGNATED WITH INORGANIC ION-EXCHANGERS

SOLVENT SYSTEM	SEPARATION ACHIEVED	PAPER	REFERENCE
	Amino Acid		
Butanol + Acetic acid (5:1)	Valine-Proline-Serine, Phenylanine-Proline-Serine, Leucine-Proline-Lysine	Titanium Arsenate	(261)
Butanol + Acetic acid + water (5:1:4)	Leucine-Valine-Histidine Tryptophan-Valine-Histidine	"	
Butanol saturated with ammonium acetate pH (2.0)	Citrulline-Proline, Histidine-Valine, Tyrosine-Leucine, Lysine-Proline-Phenyl glycine, Lysine, Proline, Phenyl alanine	Stannic Arsenate	(262)
Butanol saturated with ammonium acetate (pH 4.0)	-analine-N-phenyl alanine, 3,4,Dihydroxyphenyl alanine-N-phenyl alanine, -alanine-B-(1-Naphthyl) alanine-Dimethyl isoleucine-Leucine	"	(262)
	Phenols		
5.0×10^{-3} M $NaNO_3$	-naphthol from salicylic acid, Pyrogallol Catechol and 1 -pyridyl-2-azo Naphthol -nitroso- -Naphthol from Catechol, Pyrogallol Salicylic acid, Bromothymol red and 1-pyridyl-2-azo Naphthol	Stannic Molybdate	(260)

TABLE III (Continued)

SOLVENT SYSTEM	SEPARATION ACHIEVED	PAPER	REFERENCE
	PHENOLS		
1.0×10^{-2} M $NaNO_3$	Pyrocatechol from phenyl fluorone 1-nitroso-2-Naphthol, o-cresol, 8 hydroxy-quinoline and -Naphthol	Stannic Molybdate	(260)
1.5M $NaNO_3$	1-Pyridyl-2-azo naphthol-pyrocatechol- 1-nitroso-2-naphthol Phenol-1-nitroso-2-naphthol-picric acid, 4-(p-nitrophenyl) azo resorcinol-picric acid, B-nitroso-naphthol-1-nitroso-2-naphthol, Phenyl fluorone-1-nitroso-2-naphthol -nitroso- -Naphthol-Picric acid	•	

Spectroscopy is an important technique for the determination of substances at low level of concentration or at trace analysis level. It may be divided into various types e.g. ultraviolet, visible, I.R., Raman etc.

A rather new approach is the development of atomic absorption spectroscopy which was first suggested by Walsh in 1955 and by Alkemade and Milatz (263). Since that time it has since found its place with other important analytical techniques specially in routine analysis. It involves the study of absorption of radiant energy by neutral atoms in the gaseous state. Transition energies are unique for each element, therefore, analytical methods based on this type of absorption are highly specific. The important feature of this analysis is to employ a source of radiation that emits a line of the same wavelength as that to be used for the absorption analysis. At present this technique provides a sensitive means for the determination of more than 60 elements.

Although the atomic absorption spectrum of each element is unique to that species, unfortunately, this specificity is not always free from interferences. Lines may develop with the lines of the element being determined. Sometimes the height of an absorption peak for a metal may be influenced by the type and concentration of anions in the sample solution.

In geochemical analysis it is often necessary to determine

trace metals in rocks. Modern analytical techniques like atomic absorption spectroscopy has been applied for their direct determinations. There is necessity for modifications which are being developed to take care of interferences. For example determinations of Be by atomic absorption spectrometry suffers the interferences of calcium. Such interferences cause low accuracy and low precision in these determinations (264). The accuracy, precision and possibility of removing interferences can be increased by a prior ion-exchange separation.

Within only a couple of decades ion-exchange has become one of the most important techniques for delicate separations in analytical and preparative inorganic chemistry. Ion-exchange has played an important role in the separation of rare earths in the isolation and identifications of transuranic elements and for the enrichment of isotopes.

Most of the ion-exchange operations, whether in the laboratory or in the industries, are carried out in columns. Column operation is better than batch process, particularly for separations, as in column separations a new theoretical plate comes in contact every time when the solution is passed through a bed of ion-exchange beads where its composition is changed by ion-exchange, while in the batch operation, the complete separation may not always be possible as the equilibrium is to be maintained in the system and the equilibrium is based on the

distribution coefficient of the constituent present in the sample solution.

The present work deals with the chromatographic separation of phenols impregnating zinc silicate on Whatmann No. 3 papers. Some interesting binary and ternary separations were achieved on these loaded papers. R_f values for different phenols were also studied. A new inorganic anion-exchanger, aluminium triethanol amine was synthesized. Its properties and applications in the separation of anions of interest were studied. A new chelate ion-exchanger, thorium triethanol amine, exhibiting both cation and anion-exchange properties was synthesized. Its properties were studied and separations of some cations and anions were achieved. A new method for the separation of trace elements present in standard rock samples and dolomite sample, was achieved by making use of the combined effect of atomic absorption and ion-exchange.

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CHAPTER - II

ZINC SILICATE AS A NEW ADSORBENT FOR PAPER CHROMATOGRAPHIC SEPARATION OF PHENOLS

Paper chromatography has long been used as a simple rapid and elegant method of separation. Very difficult and time consuming separations by classical methods can be achieved clearly and in very short time by this technique. Martin has published a series of papers on the theoretical approach of this technique. But the mechanism of paper chromatography is still ambiguous. In some cases it is not possible to decide whether the mechanism is partition or adsorption between two liquid phases. Cellulose plays an important role as it possesses some ion-exchange properties. After the discovery of synthetic inorganic and organic exchangers this technique has received more attention. The ion-exchange by cellulose plays a secondary role when the papers are impregnated with some ion-exchangers and thus papers impregnated with an ion-exchanger combine the advantages of ion-exchange, adsorption and partition.

Some interesting possibilities for the separation of alkaloids and amino acids on zirconium phosphate papers have been reported (1,2). Efforts have been made for finding out a suitable adsorbent for the separation of different phenols by many workers recently (3,4). Many authors have studied the chromatography of the phenols on plain papers (5-8). Clark suggested the use of ion-exchange papers for the separation of phenols (9). Most of the sorbents used earlier either interfered with the detection of phenols applied or lacked adequate

resolution of different components present in a mixture. Stannic Molybdate (10), an inorganic ion-exchanger has been employed as adsorbent for paper chromatographic separation of phenols. Though they are good for separation purposes the invariable elongation of spots has been a negative point. In our present studies we have used zinc silicate as a potential adsorbent for the phenols. The spots obtained are compact and distinct.

EXPERIMENTAL

Apparatus

Chromatography was achieved on Whatmann No. 3 paper strips of 14 x 3 cms using glass jars, measuring 20 x 5 cms.

Reagents

Chemicals and solvents were of E.Merck (Darmstadt) and B.D.H. analar grade. Zinc nitrate (B.D.H.) and sodium silicate (Riedel,Germany) were used. Phenolic solutions were prepared by dissolving 0.1 gm of each phenol in 100 ml of distilled alcohol.

Developer

Ammonium hydroxide of different concentrations were used.

Detector

One part of mercury was dissolved in one part of fuming nitric acid and diluted with two parts of water. This reagent was used as detector. Ferric nitrate solution was also used for the detection of some phenols.

Preparation of Ion-Exchange Papers

Aqueous solutions of zinc nitrate (0.25 M) and sodium silicate were prepared. Paper strips of required size (11 cms x 3)

were first dipped in zinc nitrate solution for 3-5 seconds. The excess of the reagent was removed by placing the strips over ordinary filter sheet and allowing them to dry for 15 minutes at room temperature. The strips were then dipped in sodium silicate solution for about 5 seconds. The excess of the solution was allowed to drain off and the strips were placed over a filter sheet. These strips were dried at room temperature and then washed twice with distilled water to remove the excess of the reagents. Finally these were dried at room temperature and used as such for chromatography.

Procedure

One or two spots of test solutions were placed on the paper strips with the help of thin glass capillaries. The paper was conditioned for about 15 minutes and the solvent was then allowed to ascend (11 cms in every case).

RESULTS

A small drop of phenol solution was placed on a paper impregnated with zinc silicate. The chromatography of 27 phenols was achieved in ammonium hydroxide solutions (1 x 10^{-2}M, 1 x 10^{-1}M, 5 x 10^{-1}M and 1 M) on zinc silicate papers. The results are summarized in Table 1.

For comparison phenols were chromatographed on untreated Whatmann No. 3 papers in the aforesaid solvent systems. R_F values on plain papers are reported in Table 2. Thus a new term R_i (11) was calculated by substracting R_F value for untreated Whatmann No. 3 from R_F value for treated papers. R_i values of 26 phenols are given in Table 3.

Separation

Separations were tried for the phenols having appreciable difference in their R_F values. Spots of the mixtures were placed on the chromatographic papers and developed with the desired developer. Those practically achieved are reported in Table 4.

TABLE 1

R_F VALUES OF 27 PHENOLS IN DIFFERENT SOLUTIONS OF AMMONIA

SL. NO.	PHENOLS	1 x 10^{-2} M NH_4OH	1 x 10^{-1} M NH_4OH	5 x 10^{-1} M NH_4OH	1M NH_4OH
1.	Phloroglucinol	0.43	0.52	0.60	0.62
2.	α-Naphthol	0.34	0.40	0.42	0.45
3.	β-Naphthol	0.22	0.35	0.40	0.47
4.	2,4 Dinitrophenol	0.32	0.40	0.42	0.45
5.	p-Nitrophenol	0.49	0.50	0.56	0.59
6.	Catechol	0.62	0.66	0.70	0.75
7.	m-Cresol	0.00	0.00	0.00	0.00
8.	p-Cresol	0.00	0.00	0.00	0.00
9.	Phenol	0.00	0.00	0.00	0.00
10.	Resorcinol	0.42	0.51	0.54	0.60
11.	Gallic acid	0.10	0.20	0.27	0.32
12.	o-Nitrophenol	0.07	0.08	0.07	0.08
13.	m-Nitrophenol	0.45	0.50	0.54	0.57
14.	Xylenol	0.59	0.67	0.70	0.72
15.	Quinhydrone	0.45	0.60	0.65	0.70
16.	Quinol	0.51	0.60	0.64	0.70
17.	Picric acid	0.65	0.68	0.71	0.74

TABLE 1 (Continued)

SL. NO.	PHENOLS	1×10^{-2} M NH_4OH	1×10^{-1} M NH_4OH	5×10^{-1} M NH_4OH	1N NH_4OH
18.	Vanilline	0.54	0.58	0.59	0.64
19.	Pyrogallol	0.28	0.34	0.42	0.51
20.	Bromothymol blue	0.63	0.68	0.69	0.73
21.	Di (2-hydroxyphenylimino) ethane	0.00	0.02	0.05	0.09
22.	8-Hydroxy 7-iodoquinoline 5-sulfonic acid	0.68	0.70	0.73	0.76
23.	Phenyl fluorone (9-phenyl 2,3,7 -trihydroxy 6-fluorone)	0.00	0.00	0.01	0.03
24.	4-Chlorophenol	0.00	0.00	0.00	0.00
25.	Bromocresol green	0.66	0.72	0.74	0.81
26.	Phenolphthalein	0.41	0.56	0.60	0.65
27.	o-Aminophenol	0.53	0.63	0.66	0.70

TABLE 2

R_f VALUES OF PHENOLS ON PLAIN PAPERS IN AMMONIA SOLUTIONS

Sl. No.	PHENOLS	1×10^{-2} NH_4OH	1×10^{-1} N NH_4OH	5×10^{-1} N NH_4OH	1N NH_4OH
1.	Phloroglucinol	0.65	0.74	0.81	0.85
2.	α-Naphthol	0.41	0.54	0.57	0.60
3.	β-Naphthol	0.32	0.46	0.50	0.57
4.	2-4 Dinitrophenol	0.40	0.48	0.52	0.56
5.	p-Nitrophenol	0.55	0.60	0.62	0.65
6.	Catechol	0.82	0.87	0.91	0.95
7.	m-Cresol	0.00	0.00	0.00	0.00
8.	p-Cresol	0.00	0.00	0.00	0.00
9.	Phenol	0.00	0.02	0.02	0.04
10.	Resorcinol	0.62	0.70	0.74	0.80
11.	Gallic acid	0.56	0.57	0.58	0.65
12.	o-Nitrophenol	0.07	0.08	0.08	0.08
13.	m-Nitrophenol	0.56	0.59	0.63	0.68
14.	Xylenol	0.80	0.87	0.91	0.95
15.	Quinhydrone	0.60	0.78	0.88	0.91
16.	Quinol	0.72	0.80	0.85	0.91
17.	Picric acid	0.75	0.80	0.80	0.84

TABLE 2 (Continued)

Sl. No.	PHENOLS	1×10^{-2} M NH_4OH	1×10^{-1} M NH_4OH	5×10^{-1} M NH_4OH	1 M NH_4OH
18.	Vanilline	0.63	0.68	0.70	0.71
19.	Pyrogallol	0.60	0.65	0.70	0.79
20.	Bromothymol blue	0.70	0.77	0.80	0.83
21.	Di (2-hydroxyphenylimino) ethane	0.00	0.04	0.07	0.11
22.	8-hydroxy 7-iodoquinoline 5-sulphonic acid	0.74	0.80	0.82	0.84
23.	Phenyl fluorone (9-Phenyl 2,3,7 -trihydroxy 6-fluorone)	0.00	0.00	0.04	0.04
24.	4-Chlorophenol	0.00	0.00	0.00	0.00
25.	Bromocresol green	0.80	0.88	0.88	0.94
26.	o-Aminophenol	0.66	0.72	0.79	0.82

TABLE 3

R_f VALUES OF 26 PHENOLS

SL. NO.	PHENOLS	1 x 10^{-2} M NH_4OH	1 x 10^{-1} M NH_4OH	5 x 10^{-1} M NH_4OH	1 M NH_4OH
1.	Phloroglucinol	0.22	0.22	0.21	0.23
2.	-Naphthol	0.07	0.14	0.15	0.15
3.	-Naphthol	0.10	0.11	0.10	0.10
4.	2,4 Dinitrophenol	0.08	0.08	0.10	0.11
5.	p-Nitrophenol	0.06	0.10	0.06	0.06
6.	m-Cresol	0.00	0.00	0.00	0.00
7.	Catechol	0.20	0.21	0.21	0.20
8.	p-Cresol	0.00	0.00	0.00	0.00
9.	Phenol	0.00	0.02	0.02	0.04
10.	Resorcinol	0.20	0.19	0.20	0.20
11.	Gallic acid	0.46	0.37	0.31	0.33
12.	o-Nitrophenol	0.00	0.00	0.01	0.00
13.	m-Nitrophenol	0.11	0.09	0.09	0.11
14.	Xylenol	0.21	0.20	0.21	0.23
15.	Quinhydrone	0.15	0.18	0.23	0.21
16.	Quinol	0.21	0.20	0.17	0.20
17.	Picric acid	0.10	0.12	0.09	0.10

TABLE 3 (Continued)

Sl. No.	PHENOLS	1×10^{-2} M NH_4OH	1×10^{-1} M NH_4OH	5×10^{-1} M NH_4OH	1 M NH_4OH
18.	Vanilline	0.09	0.10	0.11	0.10
19.	Pyrogallol	0.32	0.25	0.25	0.25
20.	Bromothymol blue	0.07	0.09	0.11	0.10
21.	Di (2-hydroxyphenylimino) ethane	0.00	0.02	0.02	0.02
22.	8-hydroxy 7-iodoquinoline 5-sulphonic acid	0.06	0.10	0.09	0.08
23.	Phenyl fluorone (9-Phenyl 2,3,7 trihydroxy 6 fluorone)	0.00	0.00	0.01	0.00
24.	4 Chlorophenol	0.00	0.00	0.00	0.00
25.	Bromocresol	0.14	0.16	0.12	0.13
26.	o-Aminophenol	0.13	0.10	0.13	0.12

TABLE 4

SEPARATIONS ACHIEVED ON IMPREGNATED ZINC SILICATE PAPERS

Sl. No.	SEPARATION		SOLVENT
	Of R_F	From R_F	
	Binary Separations		
1.	Phloroglucinol (0.60)	Phenol (0.00)	1 N
2.	Phloroglucinol (0.60)	m-Cresol (0.00)	"
3.	Phloroglucinol (0.60)	p-Cresol (0.00)	"
4.	Di (2-hydroxyphenylimino) ethane (0.08)	Phloroglucinol (0.61)	"
5.	Phenyl fluorene (0.00)	Phloroglucinol (0.61)	"
6.	4-Chlorophenol (0.00)	Phloroglucinol (0.60)	"
7.	p-Nitrophenol (0.58)	m-Cresol (0.00)	"
8.	p-Nitrophenol (0.59)	p-Cresol (0.00)	"
9.	p-Nitrophenol (0.59)	Phenol (0.00)	"
10.	Di(2-hydroxyphenylimino) ethane (0.08)	p-Nitrophenol (0.59)	"
11.	4-Chlorophenol (0.00)	p-Nitrophenol (0.58)	"
12.	Phenylfluorene (0.05)	p-Nitrophenol (0.58)	"
13.	m-Nitrophenol (0.55)	m-Cresol (0.00)	"
14.	m-Nitrophenol (0.55)	p-Cresol (0.00)	"

TABLE 4 (Continued)

Sl. No.	SEPARATION		SOLVENT
	Of R_F	From R_F	
	Binary Separations		
15.	m-Nitrophenol (0.55)	Phenol (0.00)	1 N
16.	Di(2-hydroxyphenylimino) ethane (0.08)	m-Nitrophenol (0.55)	"
17.	4-Chlorophenol (0.00)	m-Nitrophenol (0.55)	"
18.	Phenylfluorone (0.05)	m-Nitrophenol (0.55)	"
19.	Catechol (0.70)	Phenol (0.00)	"
20.	Catechol (0.70)	m-Cresol (0.00)	"
21.	Catechol (0.70)	p-Cresol (0.00)	"
22.	4-Chlorophenol (0.00)	Catechol (0.70)	"
23.	Di(2-hydroxyphenylimino) ethane (0.08)	Catechol (0.70)	"
24.	Phenylfluorone (0.05)	Catechol (0.70)	"
25.	Resorcinol (0.60)	Phenol (0.00)	"
26.	Resorcinol (0.60)	m-Cresol (0.00)	"
27.	Resorcinol (0.59)	p-Cresol (0.00)	"
28.	Di(2-hydroxyphenylimino) ethane (0.08)	Resorcinol (0.60)	"
29.	Phenylfluorone (0.05)	Resorcinol (0.58)	"
30.	4-Chlorophenol (0.00)	Resorcinol (0.58)	"

TABLE 4 (Continued)

Sl. No.	SEPARATION		SOLVENT
	Of R_f	From R_f	
	Binary Separations		
31.	Xylenol (0.70)	Phenol (0.00)	1 N
32.	Xylenol (0.70)	m-Cresol (0.00)	"
33.	Xylenol (0.69)	p-Cresol (0.00)	"
34.	Xylenol (0.70)	Phenylfluorone (0.05)	"
35.	Di(2-hydroxyphenylimino) ethane (0.08)	Xylenol (0.70)	"
36.	4-Chlorophenol (0.00)	Xylenol (0.70)	"
37.	Quinhydrone (0.68)	m-Cresol (0.00)	"
38.	Quinhydrone (0.68)	p-Cresol (0.00)	"
39.	Quinhydrone (0.68)	Phenol (0.00)	"
40.	4-Chlorophenol (0.00)	Quinhydrone (0.68)	"
41.	Di(2-hydroxyphenylimino) ethane (0.09)	Quinhydrone (0.68)	"
42.	Phenylfluorone (0.05)	Quinhydrone (0.69)	"
43.	Quinol (0.70)	m-Cresol (0.00)	"
44.	Quinol (0.70)	p-Cresol (0.00)	"
45.	Quinol (0.70)	Phenol (0.00)	"
46.	Di(2-hydroxyphenylimino) ethane (0.08)	Quinol (0.70)	"

TABLE 4 (Continued)

Sl. No.	SEPARATION		SOLVENT
	Of R_f	From R_f	
	Binary Separations		
47.	4-Chlorophenol (0.00)	Quinol (0.70)	1 N
48.	Phenylfluorone (0.05)	Quinol (0.68)	"
49.	Picric acid (0.75)	m-Cresol (0.00)	"
50.	Picric acid (0.75)	p-Cresol (0.00)	"
51.	Picric acid (0.72)	Phenol (0.00)	"
52.	o-Nitrophenol	Picric acid (0.72)	"
53.	Quinol (0.71)	o-Nitrophenol (0.07)	"
54.	o-Nitrophenol (0.06)	m-Nitrophenol (0.56)	"
55.	p-Nitrophenol (0.57)	o-Nitrophenol (0.07)	"
56.	o-Nitrophenol (0.07)	Phloroglucinol (0.60)	"
57.	Catechol (0.71)	o-Nitrophenol (0.07)	"
58.	Resorcinol (0.58)	o-Nitrophenol (0.07)	"
59.	Bi(2-hydroxyphenylimino) ethane (0.08)	Picric acid (0.73)	"
60.	Phenylfluorone (0.05)	Picric acid (0.72)	"
61.	4-Chlorophenol (0.00)	Picric acid (0.72)	"
62.	Vanilline (0.60)	m-Cresol (0.00)	"
63.	Vanilline (0.60)	Phenol (0.00)	"

TABLE 4 (Continued)

Sl. No.	SEPARATION		SOLVENT
	Of R_F	From R_F	
	Binary Separations		
64.	Vanilline (0.60)	p-Cresol (0.00)	1 N
65.	Vanilline (0.60)	o-Nitrophenol (0.07)	"
66.	Phenylfluorone (0.05)	Vanilline (0.60)	"
67.	Di(2-hydroxyphenylimino) ethane (0.07)	Vanilline (0.60)	"
68.	4-Chlorophenol (0.00)	Vanilline (0.60)	"
69.	Bromothymol blue (0.72)	Phenol (0.00)	"
70.	Bromothymol blue (0.72)	p-Cresol (0.00)	"
71.	Bromothymol blue (0.72)	m-Cresol (0.00)	"
72.	Bromothymol blue (0.73)	o-Nitrophenol (0.07)	"
73.	4-Chlorophenol (0.00)	Bromothymol blue (0.72)	"
74.	Di(2-hydroxyphenylimino) ethane (0.08)	Bromothymol blue (0.72)	"
75.	Phenylfluorone (0.05)	Bromothymol blue (0.72)	"
76.	Bromocresol green (0.80)	Phenol (0.00)	"
77.	Bromocresol green (0.80)	p-Cresol (0.00)	"
78.	Bromocresol green (0.79)	m-Cresol (0.00)	"
79.	Bromocresol green (0.80)	o-Nitrophenol (0.07)	"

TABLE 4 (Continued)

Sl. No.	SEPARATION		SOLVENT
	Of R_F	From R_F	
	Binary Separations		
80.	Di(2-hydroxyphenylimino) ethane (0.07)	Bromocresol green (0.79)	1 M
81.	4-Chlorophenol (0.00)	Bromocresol green (0.80)	"
82.	Phenylfluorone (0.05)	Bromocresol green (0.80)	"
83.	Phenolphthalein (0.65)	Phenol (0.00)	"
84.	Phenolphthalein (0.65)	p-Cresol (0.00)	"
85.	Phenolphthalein (0.66)	m-Cresol (0.00)	"
86.	Phenolphthalein (0.66)	o-Nitrophenol (0.07)	"
87.	4-Chlorophenol (0.00)	Phenolphthalein (0.65)	"
88.	o-Aminophenol (0.70)	Phenol (0.00)	"
89.	o-Aminophenol (0.70)	p-Cresol (0.00)	"
90.	o-Aminophenol (0.70)	m-Cresol (0.00)	"
91.	4-Chlorophenol (0.00)	o-Aminophenol (0.70)	"
92.	Phenylfluorone (0.05)	o-Aminophenol (0.71)	"
93.	o-Aminophenol (0.70)	o-Nitrophenol (0.07)	"
94.	α-Naphthol (0.32)	Bromocresol green (0.65)	0.01 M
95.	β-Naphthol (0.22)	Bromothymol blue (0.63)	"

TABLE 4 (Continued)

Sl. No.	SEPARATION			SOLVENT
	Of R_F		From R_F	
		Ternary Separations		
96.	m-Cresol (0.00)	∝-Naphthol (0.45)	Xylenol (0.75)	1 N
97.	p-Cresol (0.00)	∝-Naphthol (0.45)	Xylenol (0.75)	"
98.	Phenol (0.00)	∝-Naphthol (0.46)	Picric acid (0.75)	"
99.	4-Chlorophenol (0.00)	∝-Naphthol (0.44)	Picric acid (0.73)	"

DISCUSSION

The results presented in Table 1 show R_F values of 27 phenols on papers impregnated with zinc silicate. The spots obtained on these papers are compact and discernible while those found on untreated papers show considerable trailing. Comparison of the results shown in Tables 1 and 2 revealed that R_F values on treated papers in most of the cases are lower than that obtained on untreated papers. This shows that zinc silicate serves as a good adsorbent for phenols and its immobilization on the paper retards the movement of various phenols to different extent. On plain papers, however, there is no such retardation force and hence a high R_F value is observed on these papers.

Besides the adsorptivity, R_F values also depend on the kind of developer used. In the present studies NH_4OH in different concentrations has been used as a developer. The results show that increase in concentration of ammonium hydroxide causes increase in R_F values. Plots of R_F values vs. concentration of ammonium hydroxide are straight lines. The results are plotted in figures 1-6. This behaviour can be attributed to the high solubility of phenols in higher concentrations of ammonium hydroxide. For the similar reasons R_F values remained extremely low when water was used as a developer.

R_I values '$R_{FU}-R_{FT}$' have been determined for various

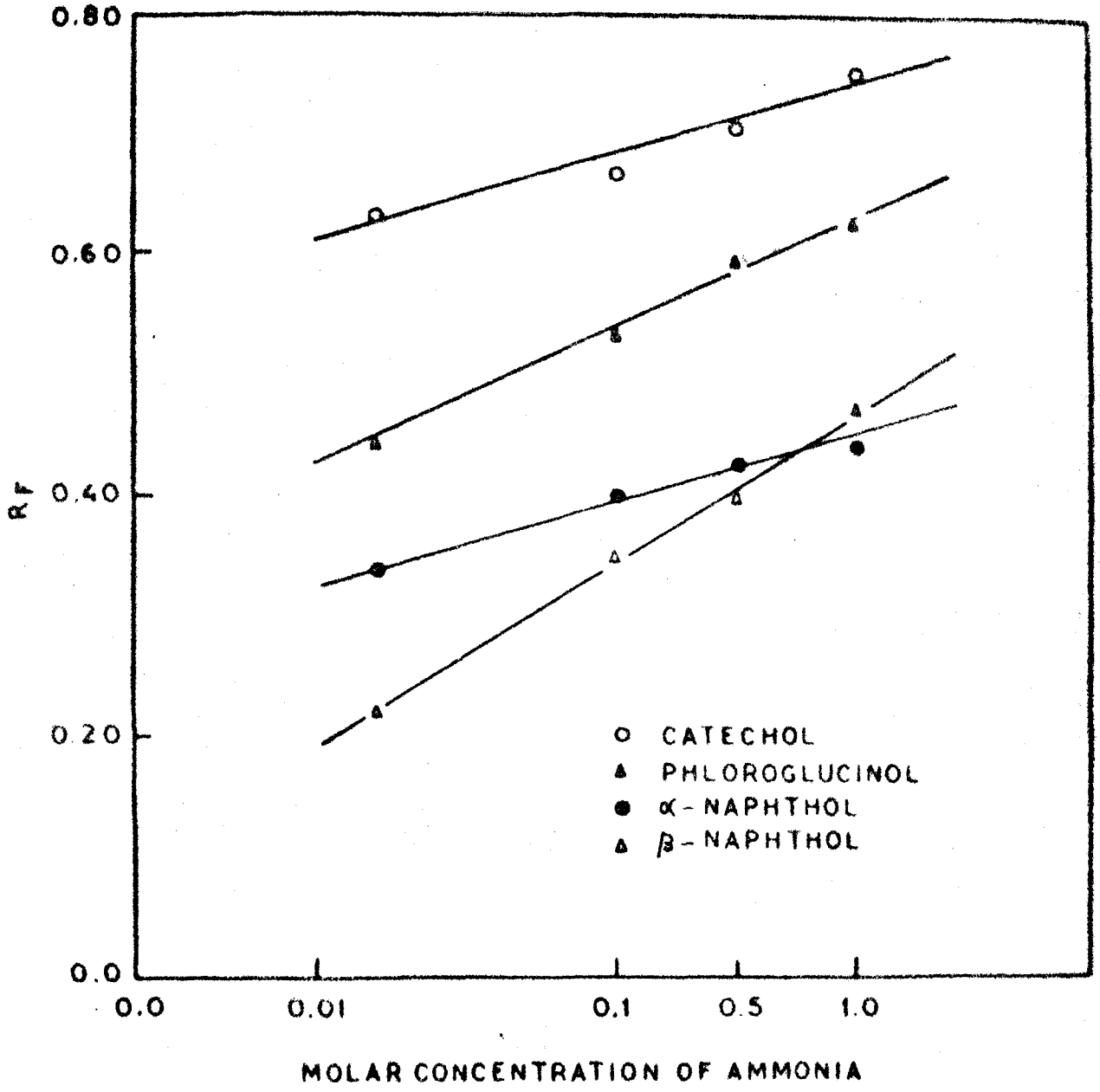

FIG. 1 PLOT OF R_F AGAINST MOLAR CONCENTRATION OF AMMONIA

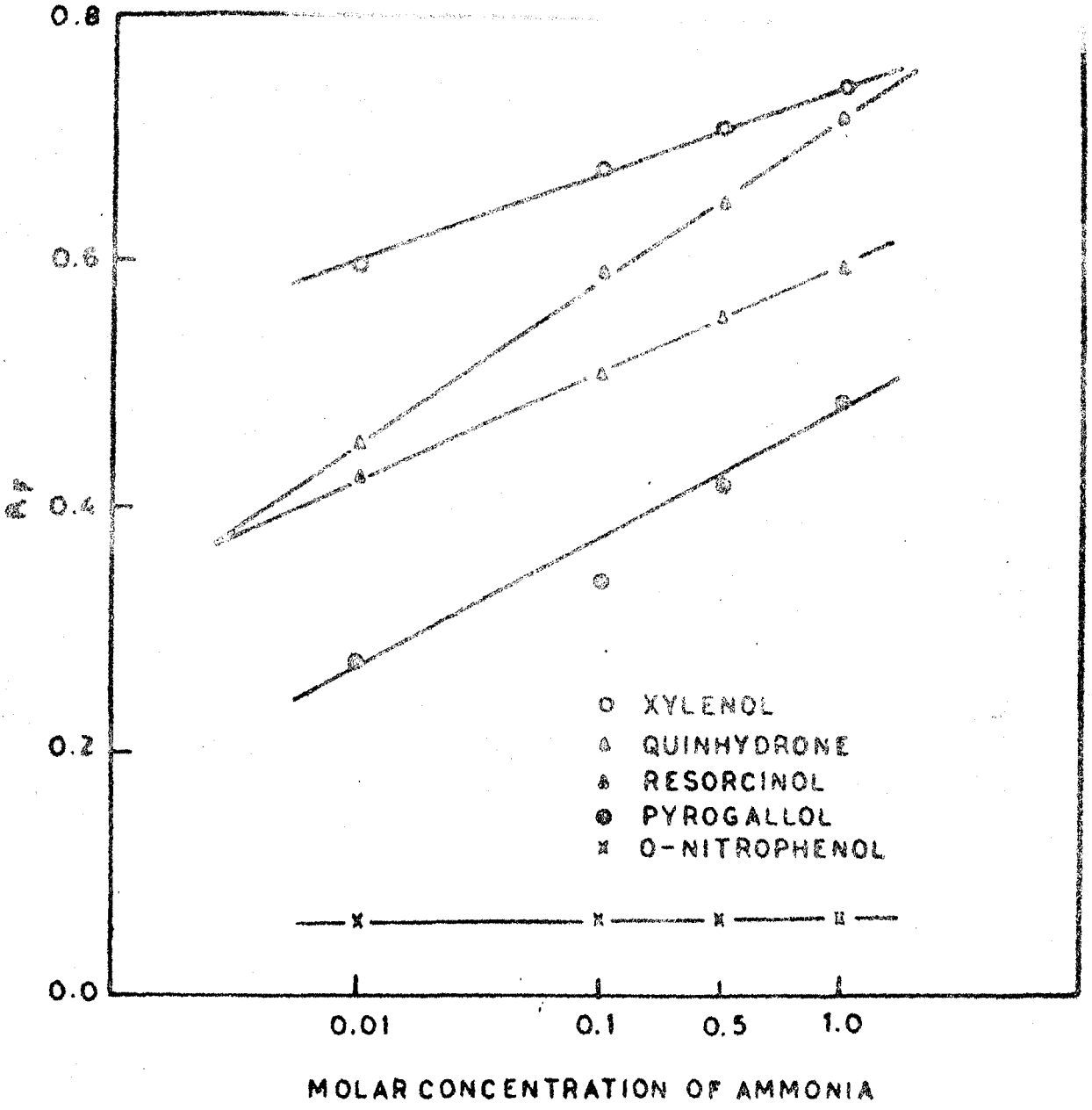

FIG. 2 PLOT OF R_F AGAINST MOLAR CONCENTRATION OF AMMONIA

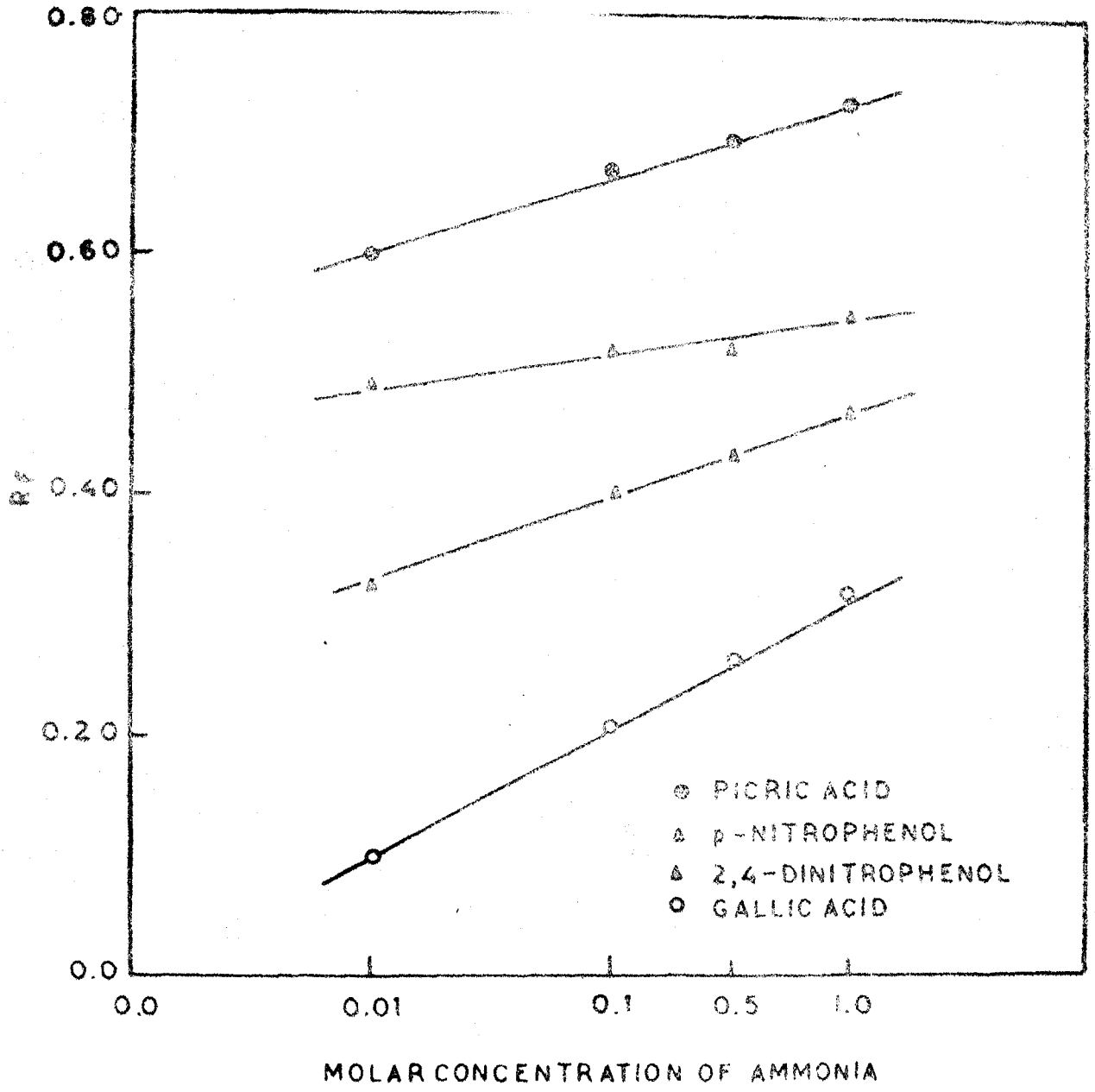

FIG. 3 PLOT OF R_F AGAINST MOLAR CONCENTRATION OF AMMONIA

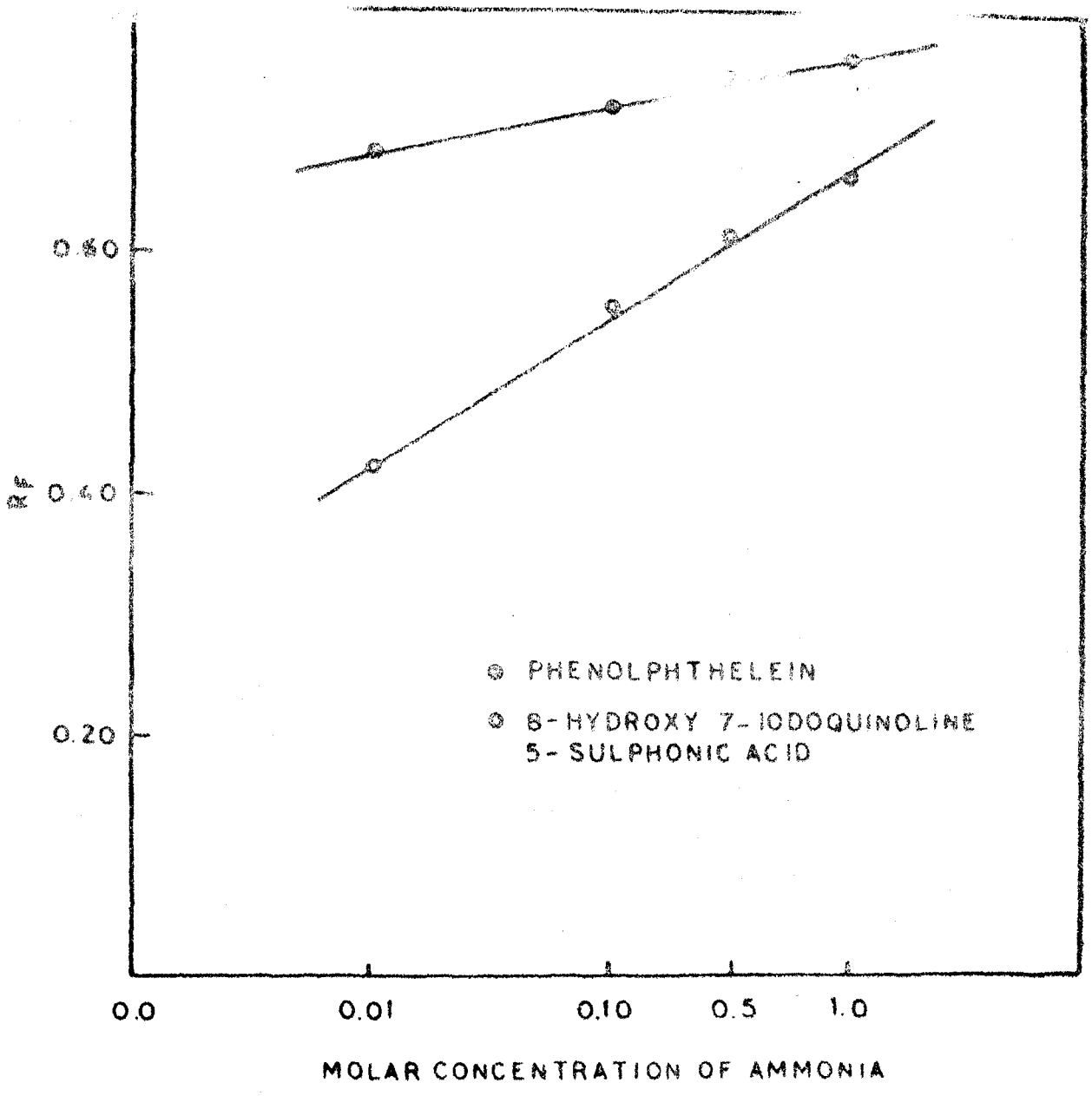

FIG. 4 PLOT OF R_F AGAINT MOLAR CONCENTRATION OF AMMONIA

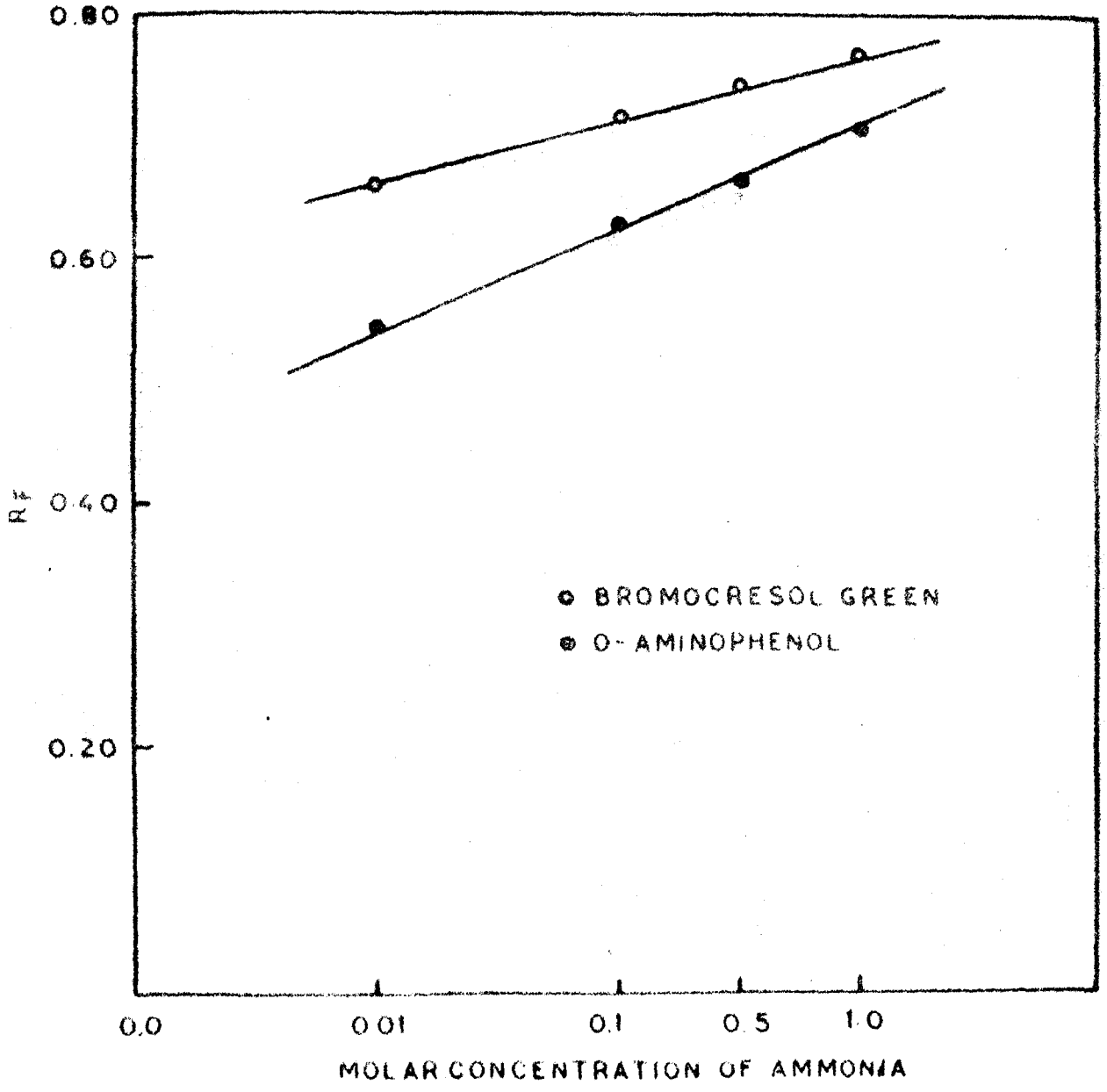

FIG. 6 PLOT OF R_f AGAINST MOLAR CONCENTRATION OF AMMONIA

phenols which measure ion-exchange effect. The results reported in Table 3 indicate that for a particular phenol R_f value remains constant for the different concentrations of ammonium hydroxide while R_f values are found to depend on the number of -OH groups present in phenol. The results are plotted in figure 7. R_f value of the phenol having three -OH groups is greater than the phenol with two -OH groups which in turn is greater than the one with one -OH group. Since zinc silicate acts as an extremely weak cation exchanger its affinity should be greater for the phenol which can furnish greater number of hydrogen ions. This possibly explains why pyrogallol is more strongly adsorbed than catechol and phenol.

The results plotted in figure 8 show the dependence of R_f values on the orientation of $-NO_2$ groups. The behaviour of ortho nitrophenol is different from that of para and meta nitrophenols. The difference in behaviour can be attributed to the possibility of intramolecular hydrogen bonding in ortho nitrophenol which is not found in either para or meta nitrophenol. R_f values have also been found to depend upon the ionisation constant of phenol. The plot of R_f vs. ionisation constant, plotted in figure 9, shows that R_f values increase with increasing ionisation constant.

Table 4 shows various separations that have been

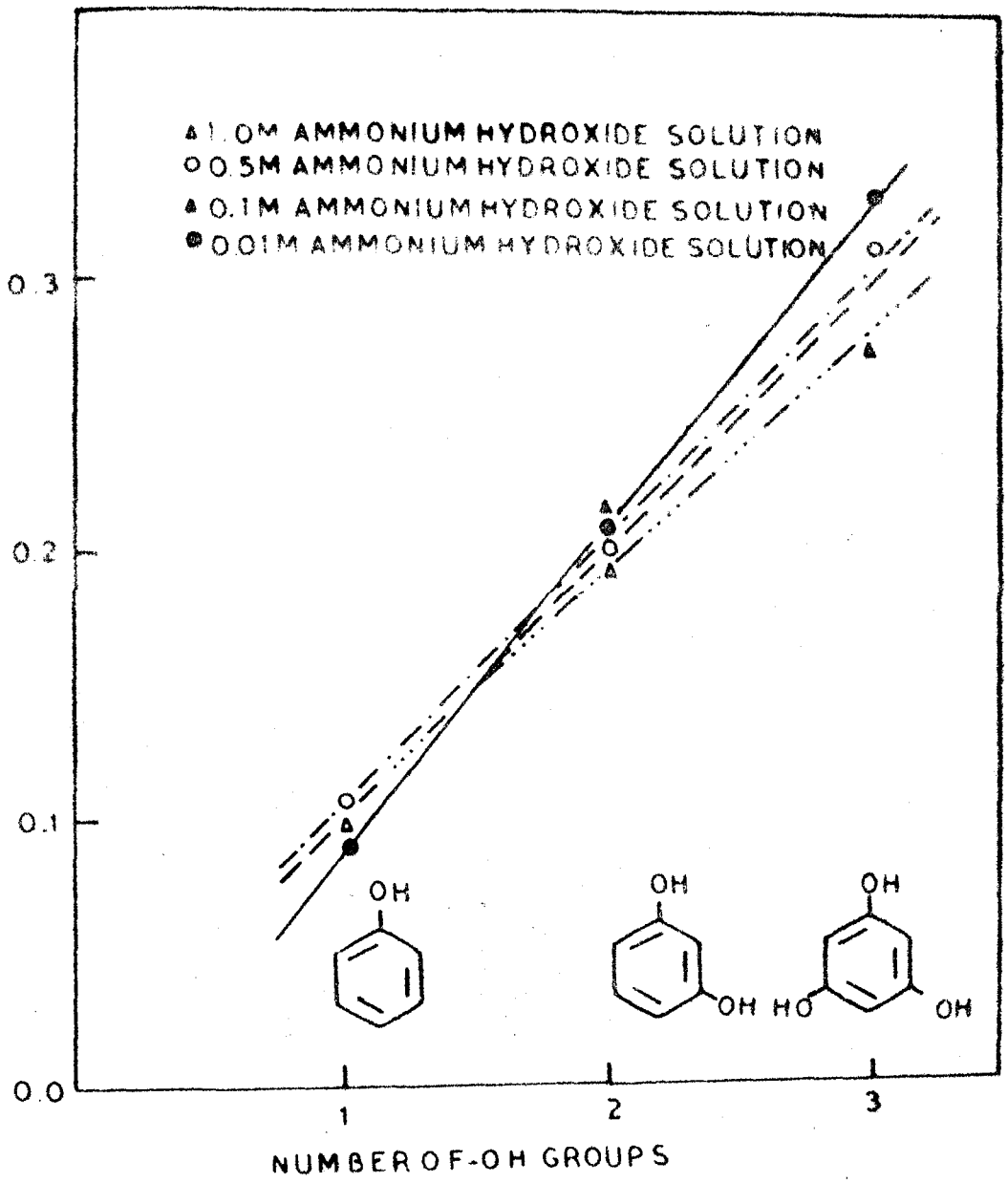

FIG. 7 PLOT OF Ri AGAINST NUMBER OF-OH GROUPS

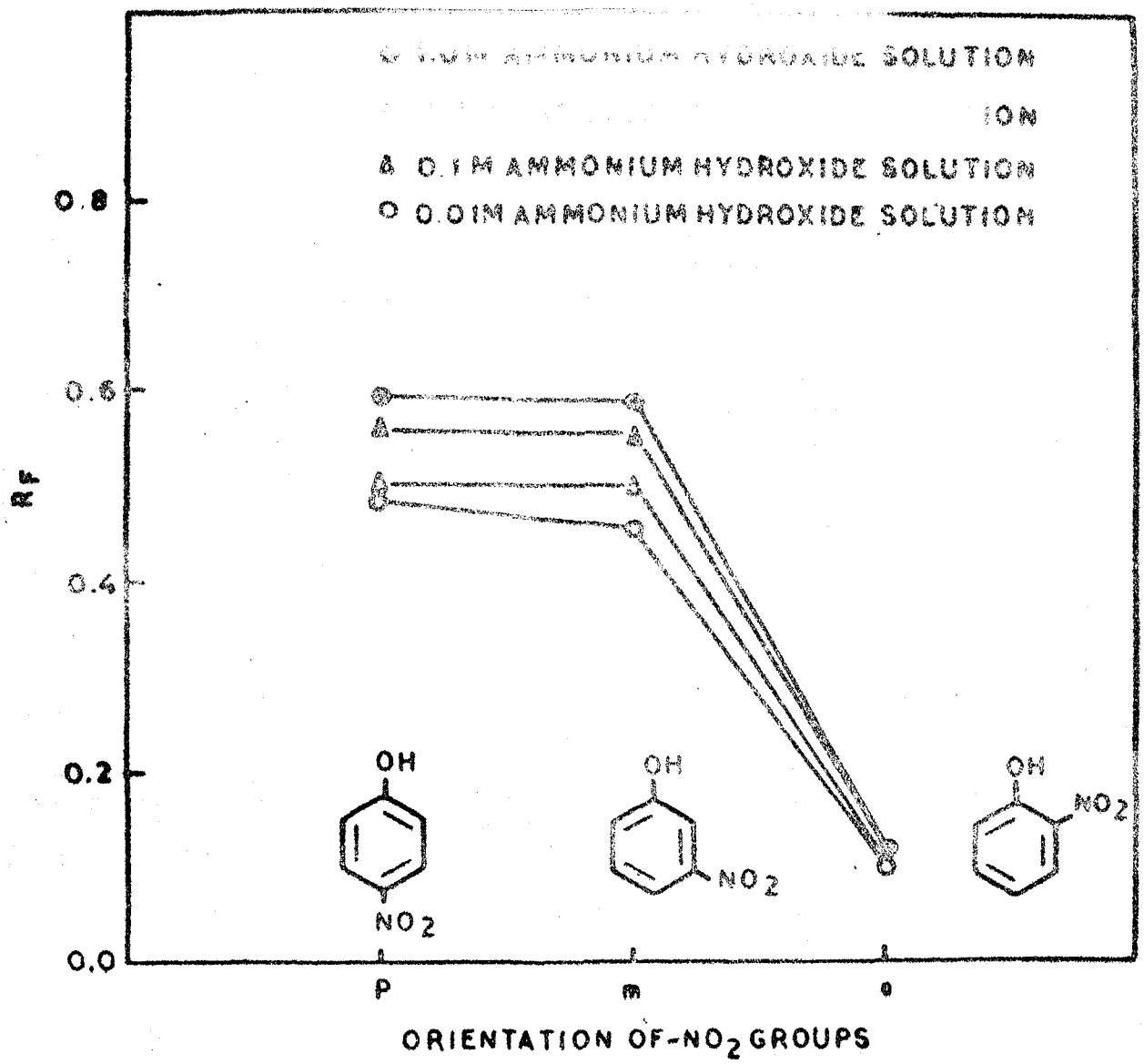

FIG. 8 PLOT OF R_F AGAINST ORIENTATION OF-NO_2 GROUPS

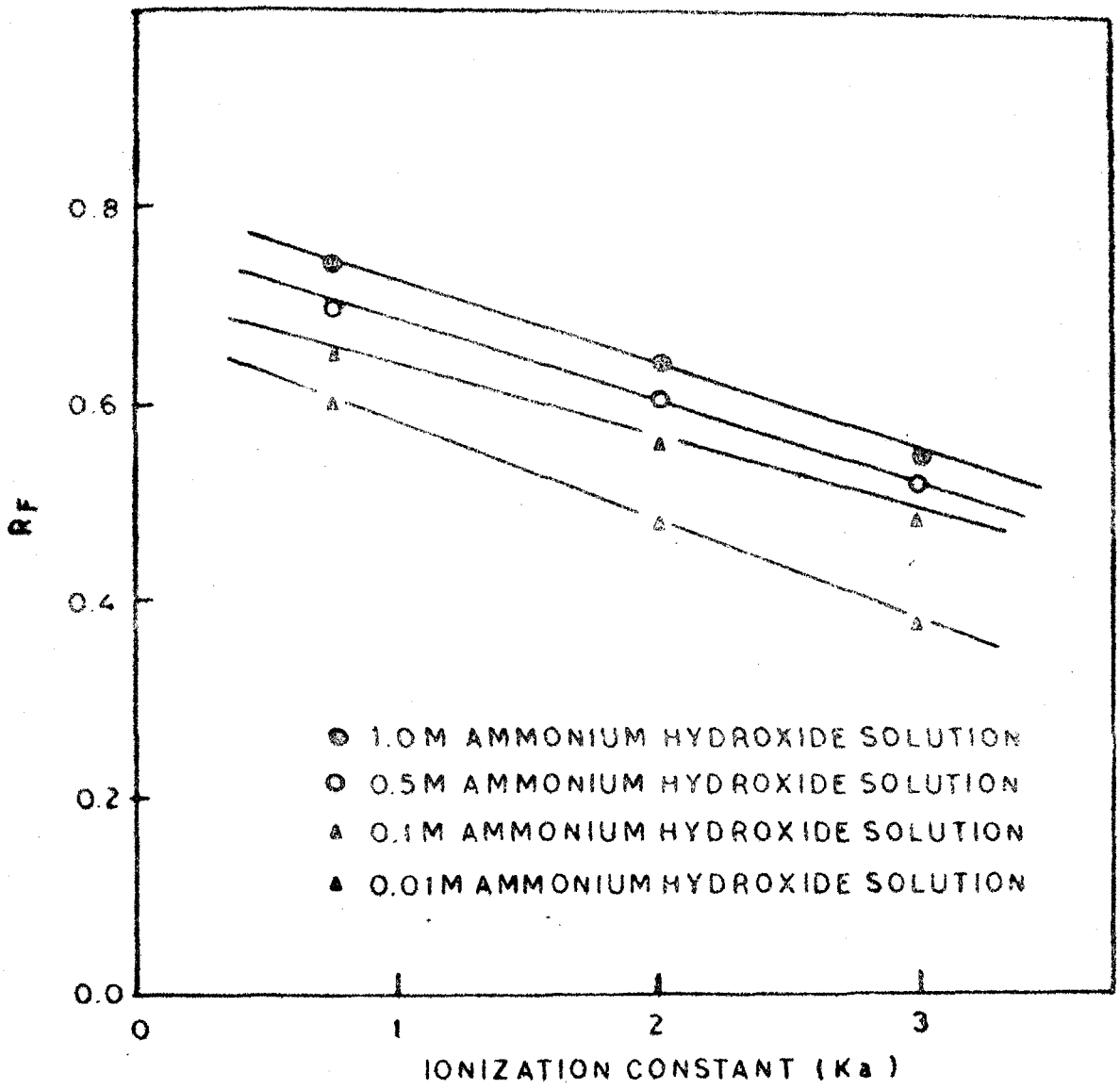

FIG. 9 PLOT OF R_F AGAINST IONIZATION CONSTANT

achieved on papers impregnated with zinc silicate. Separation of ortho nitrophenol from meta and para substituted nitrophenols can be neatly achieved. Some ternary separations have also been achieved on these papers.

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C H A P T E R - III

ALUMINIUM TRIETHANOLAMINE, A NEW INORGANIC ANION-EXCHANGER

Of various inorganic ion-exchangers reported in the literature only a few show anion exchange behaviour. The hydroxides of Sn(IV) (1), Zr(IV) (2), Al(III) (3) and others (4-5) have been found to exhibit anion exchange character in low pH range. At pH values above their isoelectric points, these materials function as cation exchangers (6). Such a limitation has severely restricted their use in the separation of different anions in basic medium. Besides, these exchangers were found lacking in their stability in basic solutions.

Efforts were, therefore, made to introduce substances containing both hydroxyl and amine groups into the matrix of metal oxides. A material of this type, Sn(IV) diethanolamine (7) was found useful for analytical separation of some cations. In the present paper the incorporation of triethanolamine group with the matrix of aluminium oxide is reported. Our studies reveal that the material not only shows anion exchange behaviour in basic medium but also possesses a good selectivity for chromate, sulphate, dichromate and thiosulphate.

EXPERIMENTAL

Reagents

Aluminium nitrate (B.D.H.) and triethanolamine (E.Merck) were used. All other chemicals were prepared by dissolving them in deionized water.

Apparatus

For spectrophotometric measurements a Metzer spectra 75 was employed. SICO shaker and Elico pH meter LI-10 were used respectively for shaking and pH measurements.

Synthesis

Aluminium triethanolamine was synthesized by mixing a 0.10 M solution of aluminium nitrate with a 0.3 M solution of triethanolamine in the volume ratio of 1:1. The mixture was kept standing for 24 hours to ensure complete precipitation. The precipitate so obtained was filtered and washed with deionized water several times. It was then dried in an oven at 40°C. The dried product was allowed to cool down and to keep at 20°C for 2 hours and then washed with deionized water. It is important that the dried sample is kept in the open at 20°C at least for 2 hours lest it tends to undergo a strong hydrolysis. After washing the material was redried at 40°C.

Table 5 shows the conditions for preparing aluminium triethanolamine exchanger.

TABLE 5

CONDITIONS OF PREPARATION OF ALUMINIUM TRIETHANOLAMINE

SAMPLE	CONDITIONS OF SYNTHESIS		MIXING VOLUME RATIO	PROPERTIES
	Molarity of reagents			
	Aluminium Nitrate	Triethanol Amine		
S-1	0.10	0.10	1:1	No precipitation
S-2	0.10	0.10	1:2	No precipitation
S-3	0.10	0.10	1:3	Thick precipitation
S-4	0.10	0.10	1:4	Mild precipitation
S-5	0.10	0.10	2:1	Mild precipitation

RESULTS

Anion Exchange Capacity

The anion exchange capacity was determined by column operation. One gram exchanger in desired form was taken on a glass wool support of a column and solutions of various anions (1 M in each case) were passed through it. The eluted anions were then determined in the effluents. The flow rate was adjusted to 0.5 ml min^{-1}. For the determination of anion exchange capacity for sulphate, the exchanger was taken in the sulphate form. The eluted sulphate ions were determined by precipitation with barium chloride and then back titrating the excess of barium ions with 0.10 M EDTA. For other anions, the exchanger was taken in chloride form and the eluted chloride ions were determined by Mohr's method. The results are given in Table 6.

TABLE 6

CAPACITY OF ALUMINIUM TRIETHANOLAMINE FOR DIFFERENT ANIONS

SL. NO.	ANIONS	CAPACITY (meq gm^{-1})
1.	Chloride	1.20
2.	Bromide	1.01
3.	Iodide	0.98
4.	Thiocyanate	1.00
5.	Thiosulphate	0.70
6.	Sulphate	1.00

I.R. Spectrum

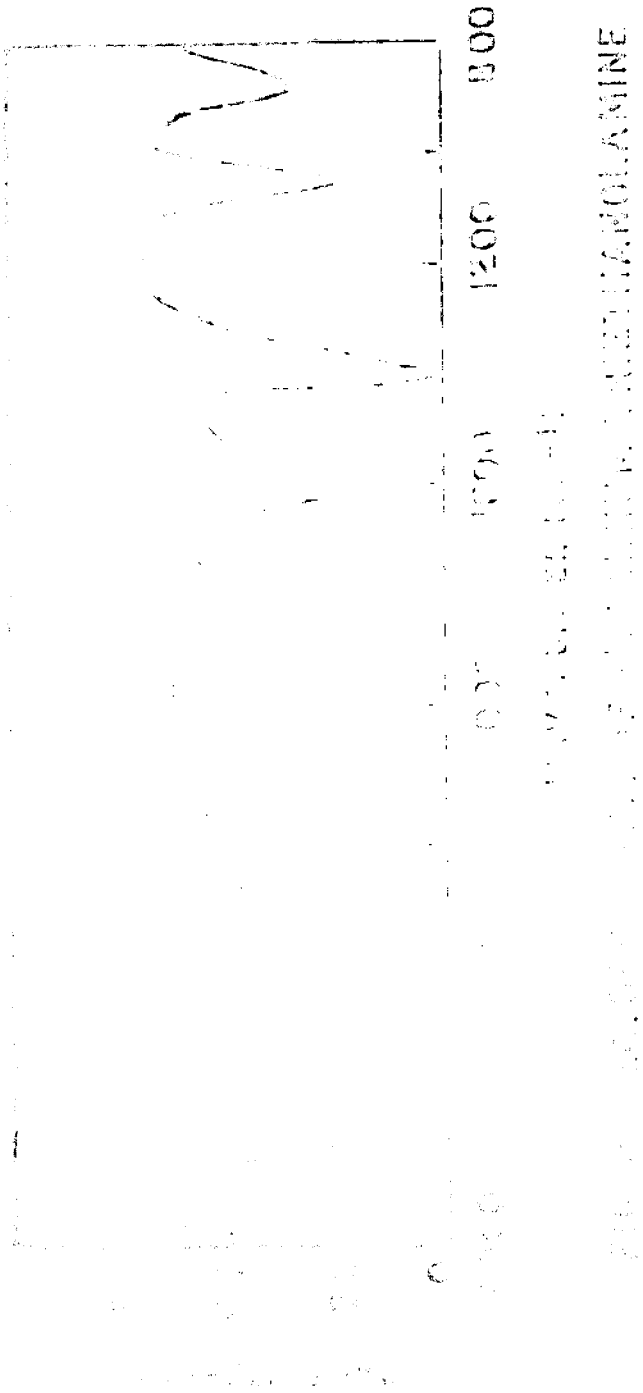
I.R. Spectrum of the sample S-III was obtained by using a KBr disc.

Composition

500 mg of aluminium triethanolamine was dissolved in 50 ml of aquaregia, evaporated to dryness, cooled and diluted to 100 ml with deionized water. Aluminium present in the solution was then determined by titrating a portion of this solution against 0.10 M EDTA solution. In the yet another portion triethanol amine was determined spectrophotometrically with 1 flouro 2,4 dinitrobenzene (8).

Qualitative Analysis

For checking the presence of different constituents, qualitative tests for aluminium (9), carbon and nitrogen (10) were performed. To check the presence of aluminium a drop of caustic alkaline test solution containing aluminate was treated with a drop of aqueous 0.1% aliazarin S and 1 N acetic acid until the violet colour disappears and then treated with a drop of acetic acid. A red colour appears in the presence of aluminium and nitrogen was detected with benzidine solution. For testing carbon, 100 mg of silver arsenate were mixed in a test tube with the solid sample to be tested. The mixture was covered with an


800
1200
MONOETHANOLAMINE

equal quantity of silver arsenate and heated for 1 hour over a burner. After cooling two drops of phosphomolybdic acid solution were added. A blue colour appears within 2 minutes. The intensity of the colour obtained depends on the quantity of oxidizable carbon in the sample.

Potentiometric Titrations

pH titrations were performed by shaking 0.5 gm of aluminium triethanolamine with a 0.1N solution of HCl with 0.1N solution of sodium chloride for 4 hours at room temperature. The mixing ratio of acid solution and its salt was taken in such a way that the total volume remained 50 ml. The pH of all the solutions were then determined. Figure 11 shows the results of pH titrations.

Recrystallization

The exchanger was first converted to chloride form by putting the exchanger in 1N sodium chloride solution for 24 hours. The exchanger was thoroughly washed with deionized water. The chloride ions were then eluted with 1N sodium nitrate solution and determined argentometrically (11). The ion-exchange capacity was calculated for chloride ions. The exhausted column after washing thoroughly with deionised water was retreated with 1N sodium chloride to remove nitrate ions and then washed with deionised water. Chloride ions were again eluted by 1N sodium nitrate to determine the ion-exchange capacity. This cycle was

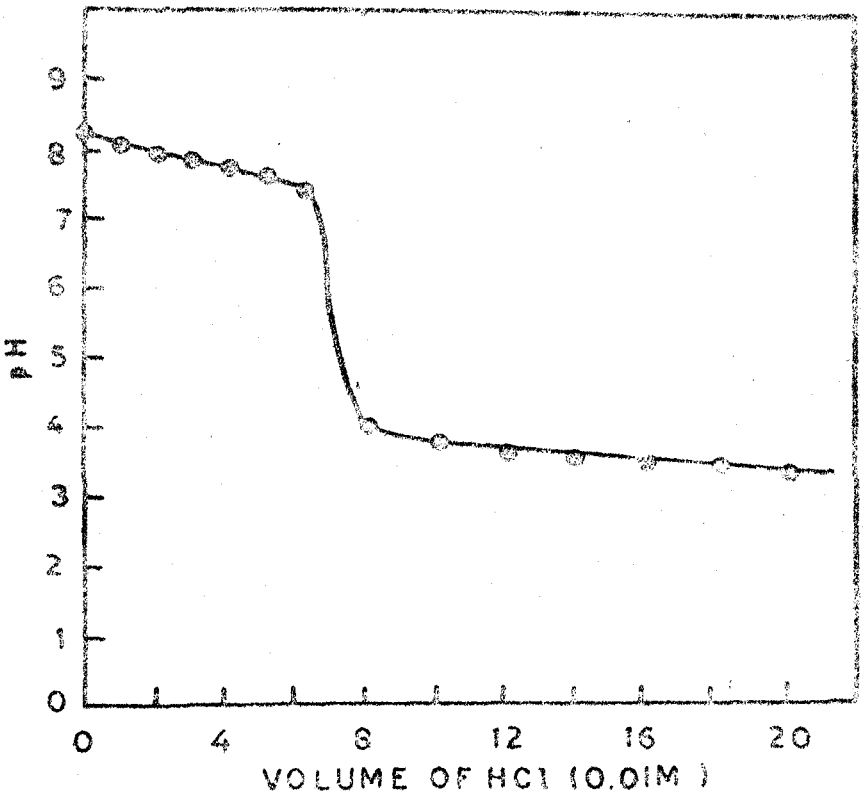


FIG. 11 POTENTIOMETRIC TITRATION CURVE ON ALUMINIUM TRIETHANOL-AMINE

repeated for five times. The anion-exchange capacity of aluminium triethanolamine sample after each cycle was found to be 1.20, 1.18, 1.14, 1.10, 1.08 meq.gm^{-1} respectively. Figure 17 shows a plot of anion-exchange capacity versus number of regeneration cycles.

Heat Treatment

Aluminium triethanolamine sample was heated at different temperatures in a muffle furnace for 2 hours. The ion-exchange capacity for thiocyanate ion was then determined by column operation. The results are presented in Table 7.

TABLE 7

CAPACITY OF THIOCYANATE IONS AT DIFFERENT TEMPERATURES

SAMPLE NO.	TEMPERATURE (°C)	CAPACITY (meq gm^{-1})
1	40	0.99
2	60	0.99
3	100	0.82
4	150	0.78
5	200	0.66
6	300	0.55

Stability

0.5 gm of aluminium triethanolamine was shaken for 4 hours in solutions in which its dissolution was to be checked. The amounts of aluminium and triethanolamine released into the supernatant liquid were then determined spectrophotometrically with aluminon (12) and ninhydrin (13) methods respectively. The results are shown in Table 8.

TABLE 8

SOLUBILITY OF ALUMINIUM TRIETHANOLAMINE

SAMPLE NO.	SOLVENT	SOLUBILITY IN mg/50 ml	
		Aluminium	Triethanol-amine
1	Deionized water	00	00
2	HNO_3 0.1M	20.25	49.00
3	H_2SO_4 0.1M	54.00	55.5
4	NaOH 0.1M	00	00
5	CH_3OH	00	00
6	C_2H_5OH	00	00
7	$HClO_4$ 0.1M	27.00	55.5
8	NH_4OH 2M	00	00
9	NaOH 1N	00	00

Distribution Studies

The distribution studies were carried out for various anions by batch process. 1 Ml of 0.1 M anionic solution was shaken for 4 hours with 500 mg of dry aluminium triethanolamine exchanger in a conical flask containing the solutions in which its dissolution was desired to be studied. The total volume was 50 ml in all cases. The supernatent liquid was drained off and the anion content remaining in the solution phase was determined. The K_d values were then calculated by the formula

$$K_d = \frac{I-F}{F} \times \frac{\text{Volume of the equilibrating solution, V ml}}{\text{Amount of exchanger, gm}}$$

where I and F are the amounts of anions before and after the equilibration. The K_d values and the solutions used are presented in Table 9.

TABLE 9

DISTRIBUTION COEFFICIENTS ON ALUMINIUM TRIETHANOLAMINE SAMPLES

SL. NO.	ANIONS	K_d ml gm^{-1}				
		D.M.W.	0.001 M NH_4OH	0.01 M NH_4OH	0.1 M NH_4OH	0.1 M NH_4OH 0.1 M NH_4NO_3
1.	Chloride	400	185	45	40	90
2.	Bromide	85	50	03	00	06
3.	Iodide	60	45	13	00	17
4.	Iodate	1400	573	73	24	59
5.	Dichromate	10400	9400	556	73	80
6.	Ferrocyanide	780	390	320	320	360
7.	Sulphite	770	146	60	55	60
8.	Bromate	360	300	245	15	15
9.	Arsenate	156	156	127	127	135
10.	Arsenite	485	409	387	181	190
11.	Sulphate	T.A.	1050	263	64	283
12.	Chromate	T.A.	T.A.	T.A.	756	760

TABLE 9 (Continued)

SL. NO.	ANIONS	K_d ml gm^{-1}				
		D.M.W.	0.001 M NH_4OH	0.01 M NH_4OH	0.1 M NH_4OH	0.1 M NH_4OH 0.1 M NH_4NO_3
13.	Thiocyanate	113	90.4	01	01	06
14.	Thiosulphate	1950	1266	720	44	127
15.	Bisulphite	611	540	100	56	95
16.	Chromate	1200	700	700	116	420
17.	Persulphate	1800	1366	325	65	16
18.	Ferricyanide	272	241	241	96	290
19.	Phosphate	T.A.	T.A.	900	90	100

T.A. = Total Adsorption

Separations

2 gm of aluminium triethanolamine was taken in a glass column having a height of 30 cm and diameter 0.69 cm. The column was washed thoroughly with deionized water and a mixture containing known amounts of anion solutions was transferred onto it. The mixture was allowed to be dissolved on the exchanger by repeated recycelization. It was seen to it that the eluted fraction contained only one component of the mixture. Table 10 depicts the quantitative separation of anions on the exchanger column.

Note

The rate determination was performed by batch process. 0.20 milliequivalents of thiocyanate was shaken with 0.5 gm of the exchanger at different intervals of time. Amount remaining in the solution was then determined. The results are plotted in figure 16.

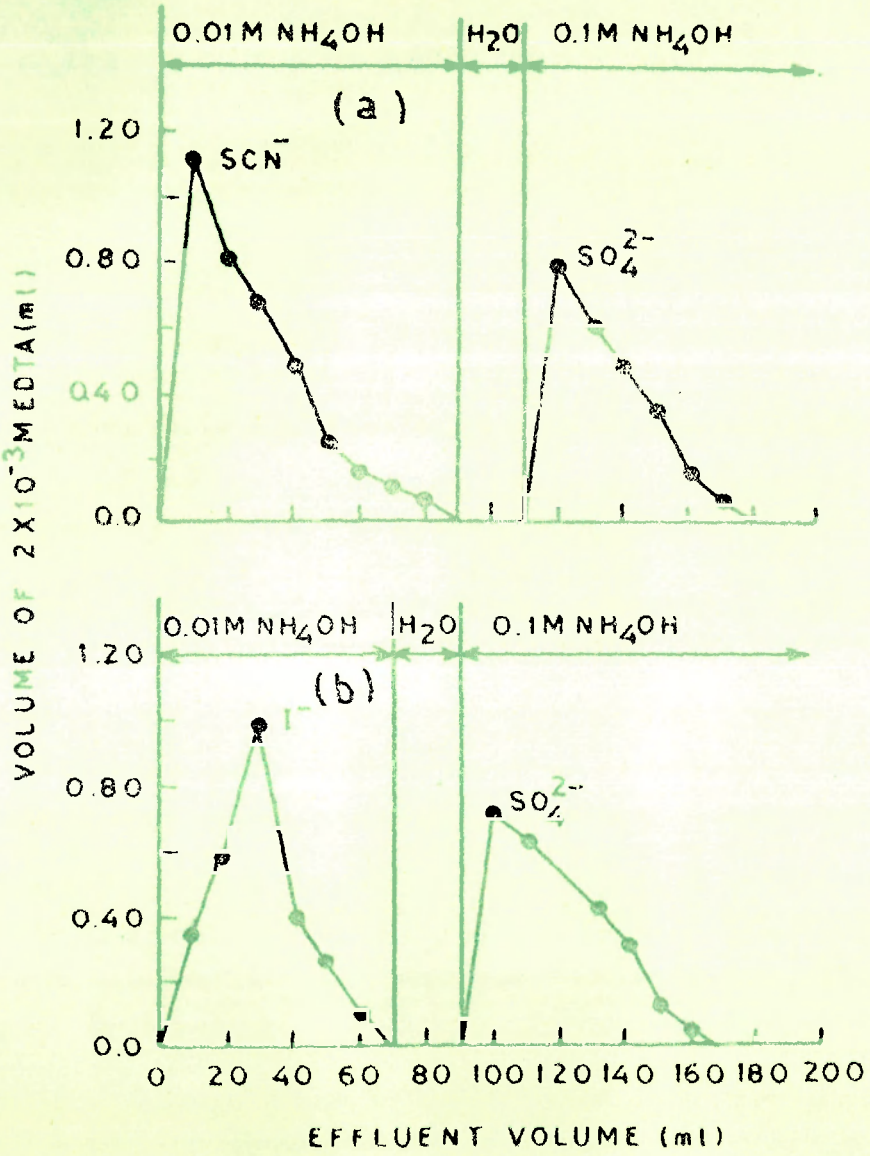


FIG. 12

(a) SEPARATION OF $SCN^- - SO_4^{2-}$

(b) SEPARATION OF $I^- - SO_4^{2-}$

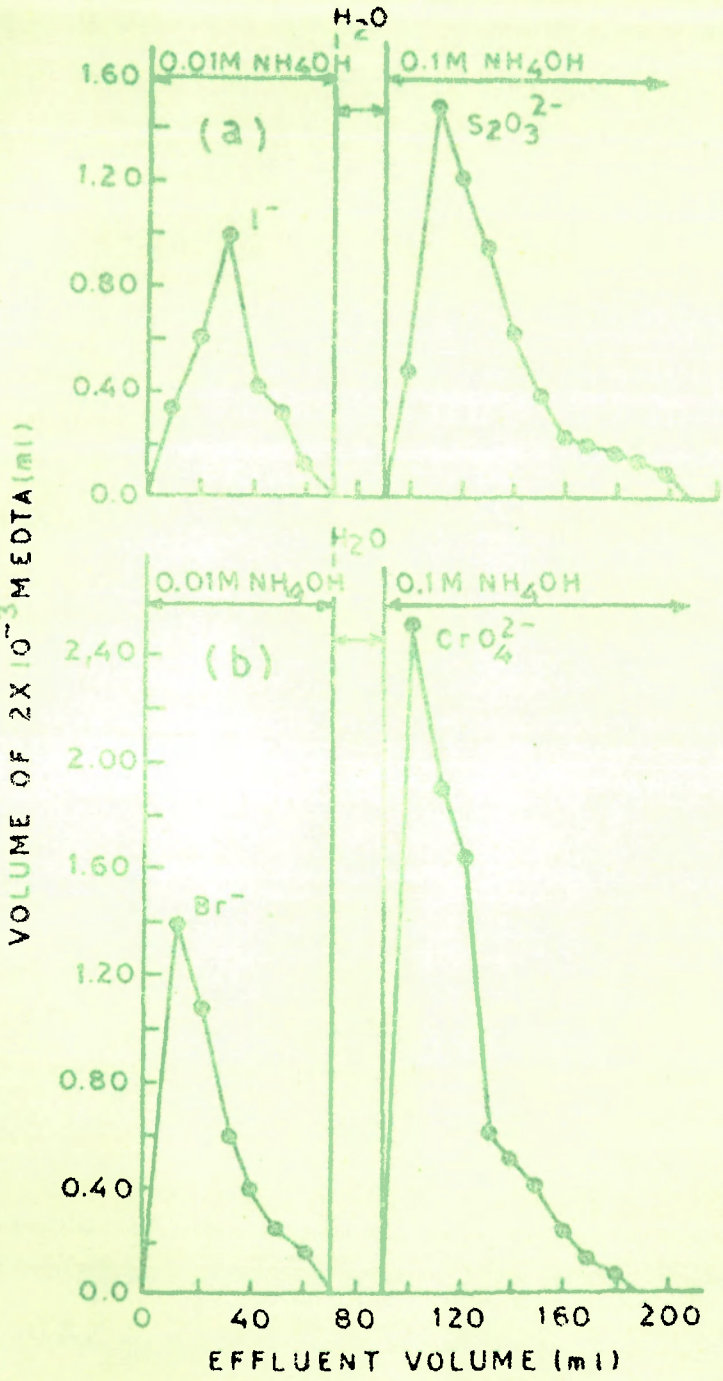


FIG. 13

(a) SEPARATION OF $I^- - S_2O_3^{2-}$

(b) SEPARATION OF $Br^- - CrO_4^{2-}$

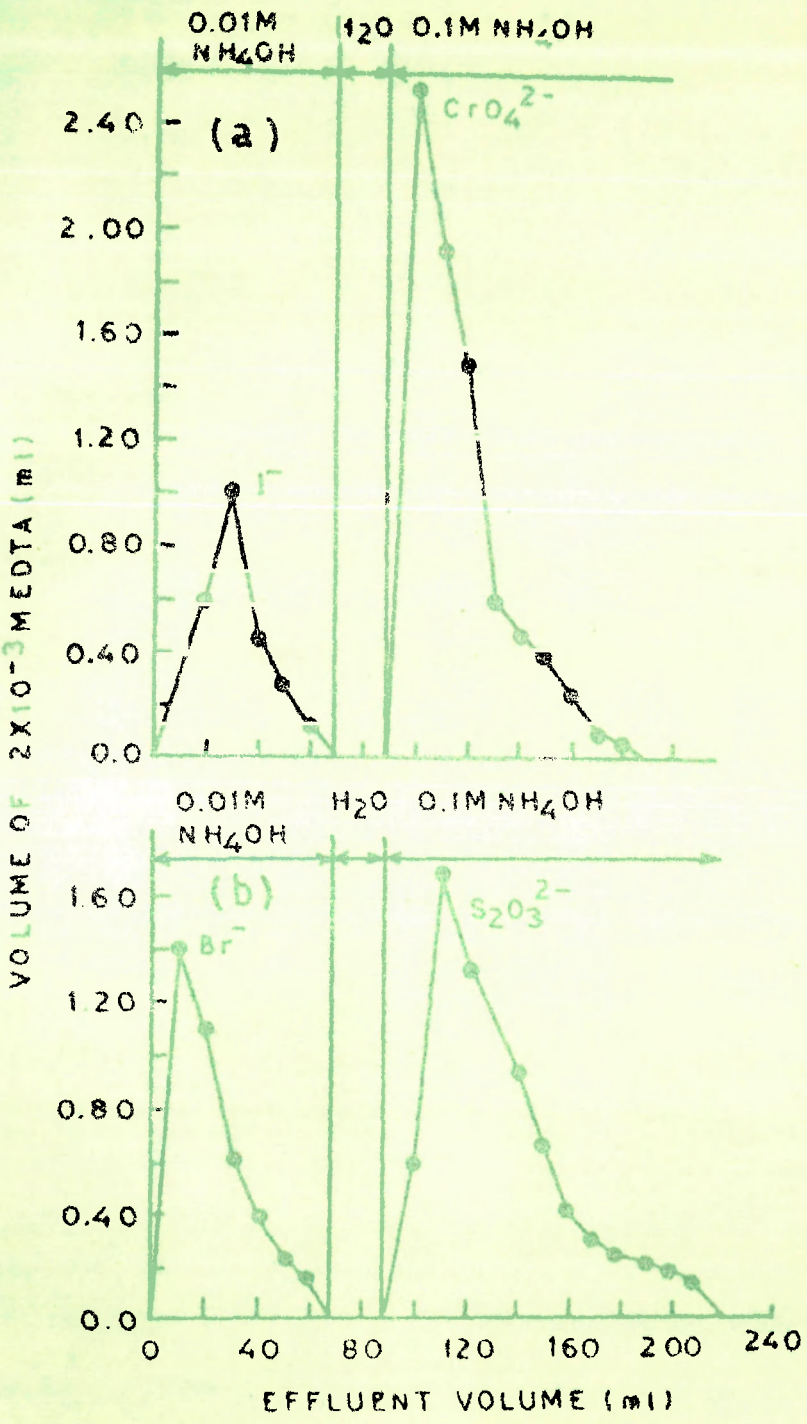


FIG. 14

(a) SEPARATION OF $I^- - CrO_4^{2-}$

(b) SEPARATION OF $Br^- - S_2O_3^{2-}$

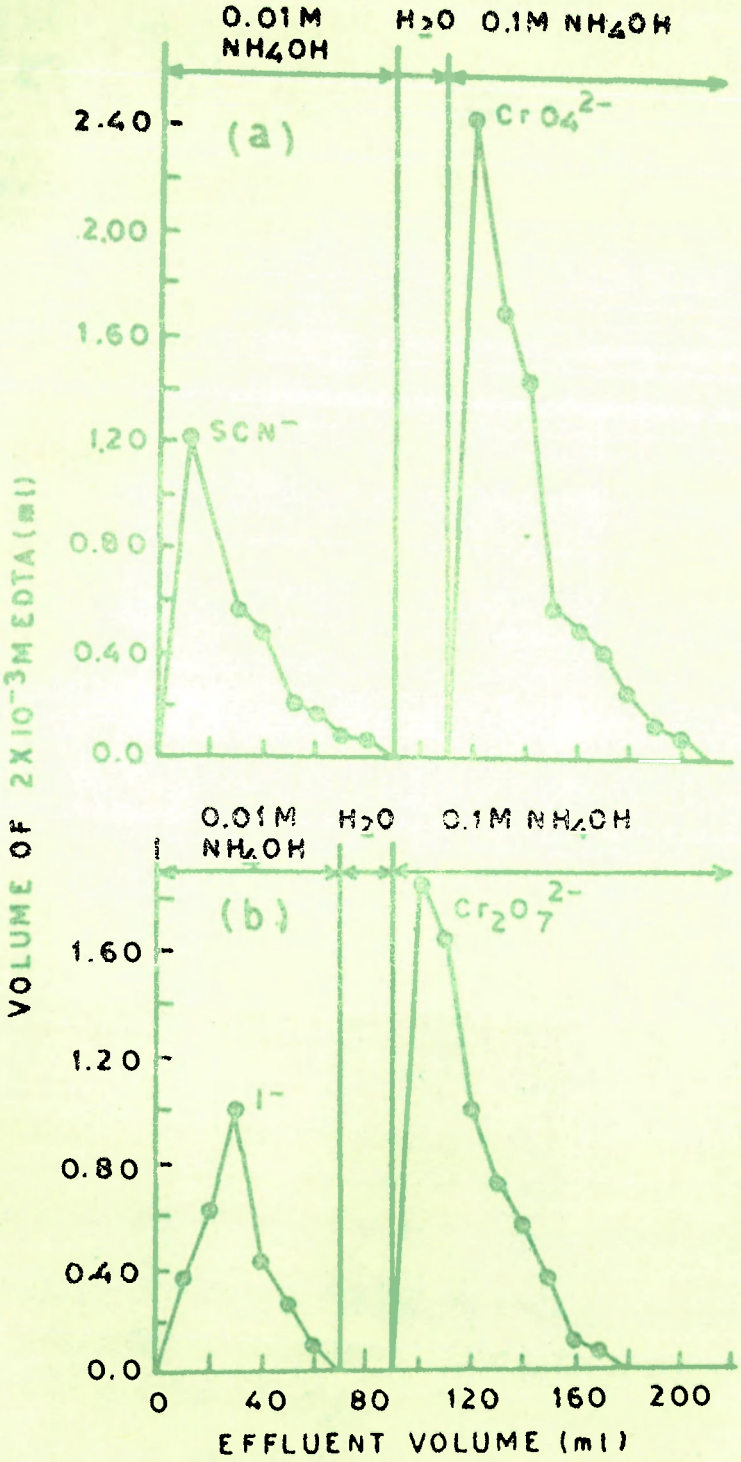


FIG. 15

(a) SEPARATION OF SCN^--CrO_4^{2-}

(b) SEPARATION OF I^--$Cr_2O_7^{2-}$

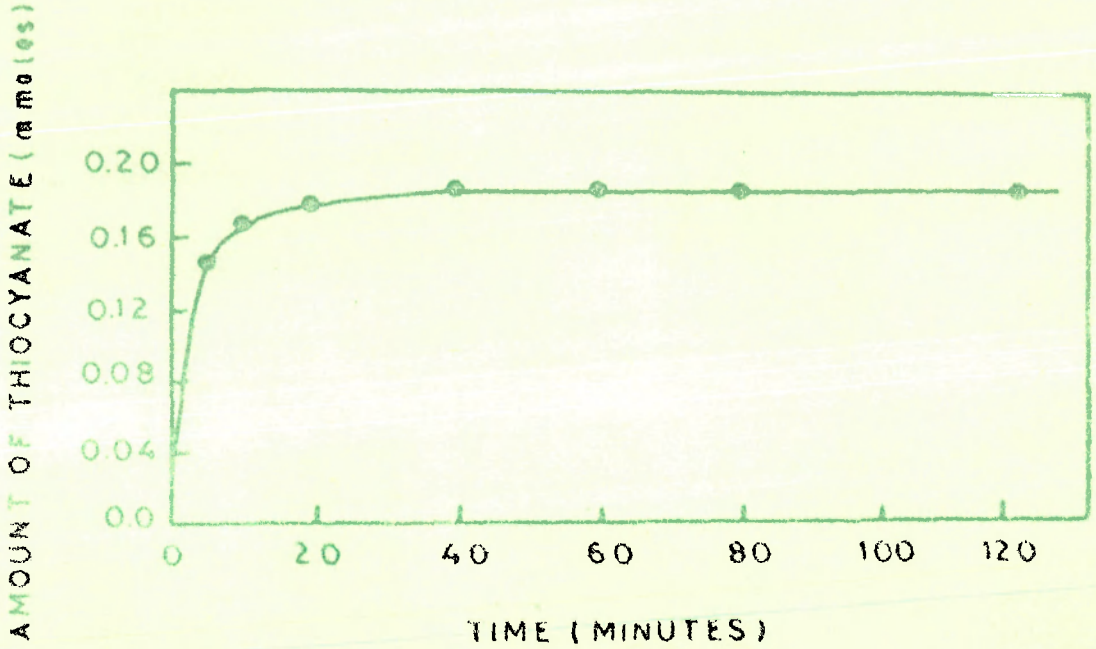


FIG. 16 RATE OF EXCHANGE FOR THIOCYANATE IONS

TABLE 10

QUANTITATIVE SEPARATION OF ANIONS ON ALUMINIUM TRIETHANOLAMINE

SAMPLE NO.	SEPARATIONS ACHIEVED	ELUENTS	AMOUNT LOADED (mg)	AMOUNT FOUND (mg)	% ERROR
1	SCN^-	0.01 M NH_4OH	2.20	2.19	0.4
	SO_4^{2-}	0.1 M NH_4OH	1.31	1.28	2.3
2	I^-	0.01 M NH_4OH	3.63	3.55	2.2
	SO_4^{2-}	0.1 M NH_4OH	1.31	1.28	2.3
3	I^-	0.01 M NH_4OH	3.63	3.58	2.4
	$S_2O_3^{2-}$	0.1 M NH_4OH	6.92	6.81	1.5
4	Br^-	0.01 M NH_4OH	3.22	3.18	1.2
	CrO_4^{2-}	0.1 M NH_4OH	9.58	9.30	2.9
5	I^-	0.01 M NH_4OH	3.63	3.55	2.2
	CrO_4^{2-}	0.1 M NH_4OH	9.59	9.51	0.8
6	Br^-	0.01 M NH_4OH	2.80	2.77	1.1
	$S_2O_3^{2-}$	0.1 M NH_4OH	6.92	6.83	1.3
7	SCN^-	0.01 M NH_4OH	2.20	2.18	1.0
	CrO_4^{2-}	0.1 M NH_4OH	9.59	9.53	0.6
8	I^-	0.01 M NH_4OH	3.63	3.58	1.4
	$Cr_2O_7^{2-}$	0.1 M NH_4OH	4.61	4.56	1.8

DISCUSSION

It can be seen from Table 5 that for precipitation of aluminium triethanolamine, the metal to amine ratio must be maintained at 1:3. Any alteration in this ratio resulted either in disappearance of the precipitate or in a mild precipitation. To check if this material retains the amine group, the qualitative tests for carbon and nitrogen were performed. The tests confirmed the presence of these elements.

Further evidence was provided by the I.R. studies. Spectrum shown in figure 10 reveals the following pattern:

(i) A broad peak ranging from 3100-3500 cm^{-1} is attributed to the -OH stretching vibration.

(ii) A peak between 2820-2980 is due to the C-H (aliphatic) stretching vibration.

(iii) C-H bending frequency due to $-CH_2-$group is observed in the frequency range 1400-1480 cm^{-1}.

(iv) A peak in the frequency range 1180-1040 cm^{-1} resembles C-N bending vibration.

(v) A peak in the frequency range 1770-1780 cm^{-1} is due to C-O stretching vibration.

(vi) A peak at 900 cm^{-1} is because of the presence of aluminium metal-oxygen bonding.

From the above observations it can be inferred that the material precipitated by aluminium nitrate and triethanolamine

still retains the amine group. The results of the composition analysis revealed that two molecules of triethanolamine are bound with one atom of aluminium. That the linkage of metal with triethanolamine occurs through oxygen atom is indicated by the presence of a C-O stretching vibration peak in IR spectrum. This was further confirmed when mixing together of aluminium nitrate solution and that of triethylamine under similar conditions showed no precipitation. Further research, however, is needed to unambiguously elucidate the formula. It can be seen from Table 6 that the anion-exchange capacity ranges from 1.0 to 1.2 meq gm^{-1} except for thiosulphate ions which has a capacity of only 0.7 meq. This may probably be due to its comparatively large ionic size. The $>N^{+}$ group incorporated with the matrix possibly accounts for the anion-exchange behaviour of this material.

Figure 17 gives a plot of ion-exchange capacity against number of regeneration cycles studied upto five cycles. The slight loss in the capacity is observed after each cycle. This suggests that the same column of the ion-exchanger may be used again and again.

The potentiometric titration curve (Figure 11) shows the material to be a monofunctional anion-exchanger.

The results of heat treatment shows that the material suffers less in its anion-exchange capacity with increase in

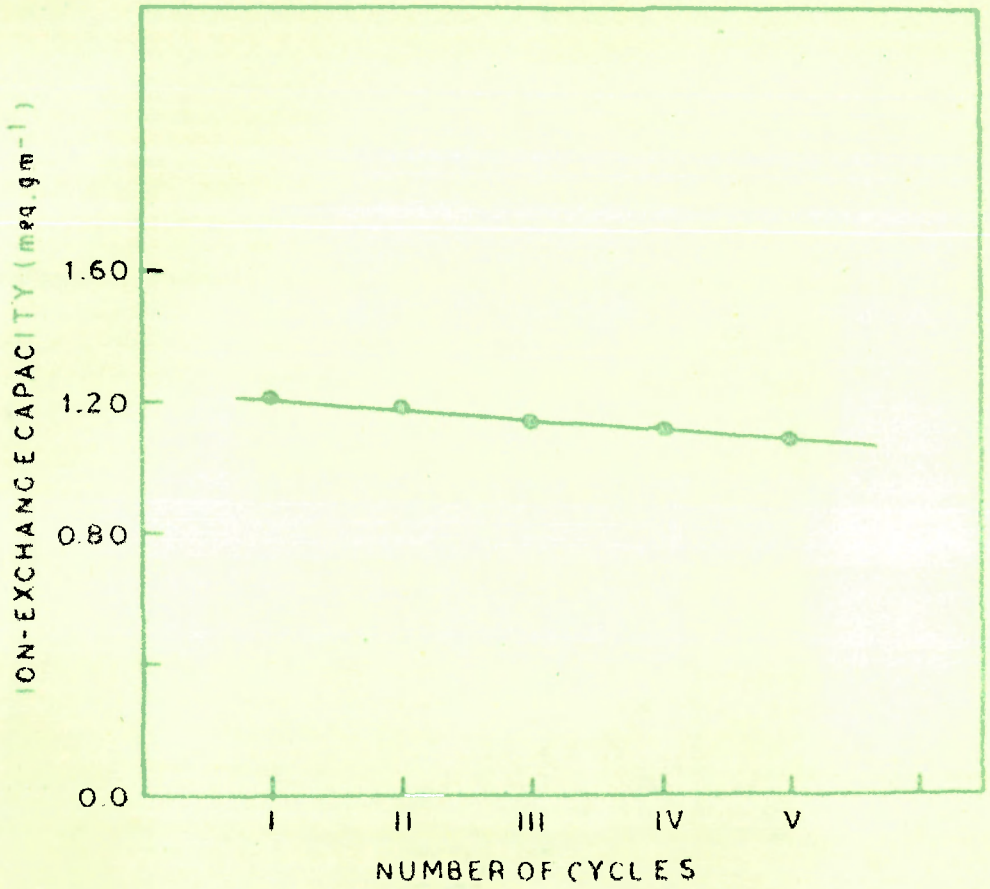


FIG.17 PLOT OF ION-EXCHANGE CAPACITY AGAINST NUMBER OF REGENERATION CYCLES (FOR CHLORIDE IONS)

drying temperature and this shows that the material aluminium triethanolamine should be used as an anion-exchanger at a temperature below 100°C.

The results reported in Table 8 for the stability of aluminium triethanolamine in various solvents show that the material is stable in organic solvents and in neutral aqueous solutions. Ammonium hydroxide and sodium hydroxide upto 2 M can be safely used. In strong acids, however, the material shows appreciable dissolution and should be avoided.

The results of the distribution behaviour of different anions on aluminium triethanol amine are presented in Table 9. It can be seen that K_d values of almost all the anions are the largest in deionized water. They, however, were appreciably lowered when a solution of NH_4OH was used for equilibration. The results also show a decrease in K_d values with increase in concentration of ammonium hydroxide. The material, being a weak anion exchanger, possesses a high affinity for hydroxyl ions and hence in its presence the other anions show little uptake.

On the basis of large differences in K_d values of various anions in different solvent systems, a number of separations were tried. The separation of SCN^- from SO_4^{2-} and CrO_4^{2-}, I^- from SO_4^{2-}, $S_2O_5^{2-}$, $Cr_2O_7^{2-}$ and CrO_4^{2-} and Br^- from CrO_4^{2-} and SrO_3^{2-} have been successfully achieved and are summarized in Table 10. The order of elution and eluents used are shown in figures 12a-15b.

The equilibrium studies plotted in figure 16 show that the equilibrium is attained in 40 minutes. Such a fast equilibrium is not observed with other inorganic ion-exchangers. It can, therefore, be inferred that the introduction of an amine group into the matrix of an inorganic metal oxide not only alters their selectivity for various anions but also brings about a fast equilibrium rate.

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CHAPTER - IV

THORIUM TRIETHANOLAMINE AS A NEW CHELATING AND AN ANION-EXCHANGER

The chelate ion-exchangers have drawn attention recently. The preparation and properties of chelating resins and their importance in separation science are reported viz. polystyrene based oxime (1,2), o-hydroxypropiophenone, oxime-divinyl benzene styrene resin (3), thioglycolate chelating resin (4), carboxylate type (5), chelating exchanger Dowex A1, N acylphenylhydroxyl amines (6). In the complexing tendency the material behaves similar to the complexing agent and the metal ion can be detached from the column leaving the complexing agent. However, the possibility has not been explored towards inorganic chelate ion-exchangers. Sn(IV) diethanolamine was found useful for the separation of some cations (7). Only few inorganic ion-exchangers reported in the literature showed anion exchange capacity. The hydroxides of Sn(IV) (8), Zr(IV) (9), Al(III) (10) and others (11-12) have been found to exhibit anion exchange behaviour in low pH range. These materials were found lacking in their stability in basic solutions. Such a limitation has restricted their use in the separation of anions in basic media. To overcome these limitations efforts were made for a chelating ion-exchanger exhibiting amphoteric character. The exchanger was prepared by incorporating triethanolamine group into the matrix of thorium oxide. The material thorium triethanolamine was not only stable in basic media but the separations of anions in basic media and that of cations with strong chelating agent were also successfully achieved.

EXPERIMENTAL

Apparatus

An electric temperature controlled SICO shaker for shaking, Bausch and Lomb spectronic 20 U.S.A. for spectrophotometric determination and Elico pH meter model LI-10 (India) for pH measurements were used.

Reagents

Thorium nitrate (B.D.H.), triethanolamine (E.Merck) were used. The other chemicals used were of analytical grade.

Synthesis

Thorium triethanolamine was prepared by mixing a 0.1 M solution of thorium nitrate and a 0.1 M solution of triethanol amine solution in different volume ratios as shown in Table 11. The precipitate was allowed to stand for 24 hours at room temperature (25-30°C). The precipitate was then washed with deionized water by decantation. It was filtered off and then dried in an oven and was kept in the air for 3 hours. The dried product broke down into small particles when immersed into water. The exchanger particles were washed and converted into the hydroxyl form by keeping in the solution of 2 M sodium hydroxide overnight intermittently replacing the supernatant liquid with a fresh sodium hydroxide solution. It was finally washed with deionized water and dried at 40°C.

TABLE 11

CONDITIONS OF PREPARATION OF THORIUM TRIETHANOLAMINE

SAMPLE	CONDITIONS OF SYNTHESIS		MIXING VOLUME RATIO	PROPERTIES
	Molarity of Reagents			
	Thorium Nitrate	Triethanol-Amine		
S-1	0.10	0.10	1:1	No precipitation
S-2	0.10	0.10	1:2	No precipitation
S-3	0.10	0.10	1:3	Mild precipitation
S-4	0.10	0.10	1:4	Thick precipitation
S-5	0.10	0.10	2:4	Mild precipitation
S-6	0.10	0.10	2:1	No precipitation
S-7	0.10	0.10	1:5	No precipitation

RESULTS

Anion Exchange Capacity

The anion exchange capacity of thorium triethanolamine was determined by column operation. The ion-exchanger weighing one gram was converted in the desired form (chloride, bromide, iodide, thiocyanate, thiosulphate, sulphate) by treating with 2M solutions of sodium/potassium/ammonium salts of different anions. The exchanger was placed in the column with glass wool support. The column was washed with deionized water thoroughly. 1.0M sodium nitrate was used as an eluent. The elution rate was maintained at 0.5 ml min^{-1}. The anion-exchange capacity for sulphate was determined by taking the exchanger in sulphate form in a glass column. The eluted sulphate ions were determined by precipitation with barium chloride and then back titrating the excess of barium ions with 0.1M EDTA solution. To determine the anion exchange capacity of halide ions the exchanger was first converted into halide form and then eluting it with 0.1M solution of potassium nitrate. The halide ions collected as effluent were determined by Mohr's method (13). The eluted thiocyanate ions were titrated against silver nitrate solution using ferric nitrate (in 4M nitric acid) as indicator. Thiosulphate ion was determined iodometrically by titration against 0.1N copper sulphate solution. The anion exchange capacity for different anions are shown in Table 12.

TABLE 12

ANION EXCHANGE CAPACITY OF THORIUM TRIETHANOLAMINE

Sl. No.	ANIONS	SALTS USED	CAPACITY (meq.gm^{-1})
1.	Chloride	Sodium chloride	0.80
2.	Bromide	Sodium bromide	0.59
3.	Iodide	Potassium iodide	0.44
4.	Sulphate	Sodium sulphate	0.25
5.	Thiosulphate	Sodium thiosulphate	0.18
6.	Thiocyanate	Ammonium thiocyanate	0.61

Recyclization

For the recyclization the exchanger was converted in chloride form by 1 N sodium chloride solution and then the anions were eluted with 1 N sodium nitrate solution. This cycle was repeated for five times. The anion exchange capacity for chloride ions after each cycle was found to be 0.80, 0.78, 0.74, 0.69 and 0.64 meq.gm^{-1} respectively. The figure 18 shows a plot of anion exchange capacity versus number of regeneration cycles.

Anion Exchange Capacity as a Function of Concentration of Eluting Reagent

Ion-exchange capacity of most of the inorganic ion-

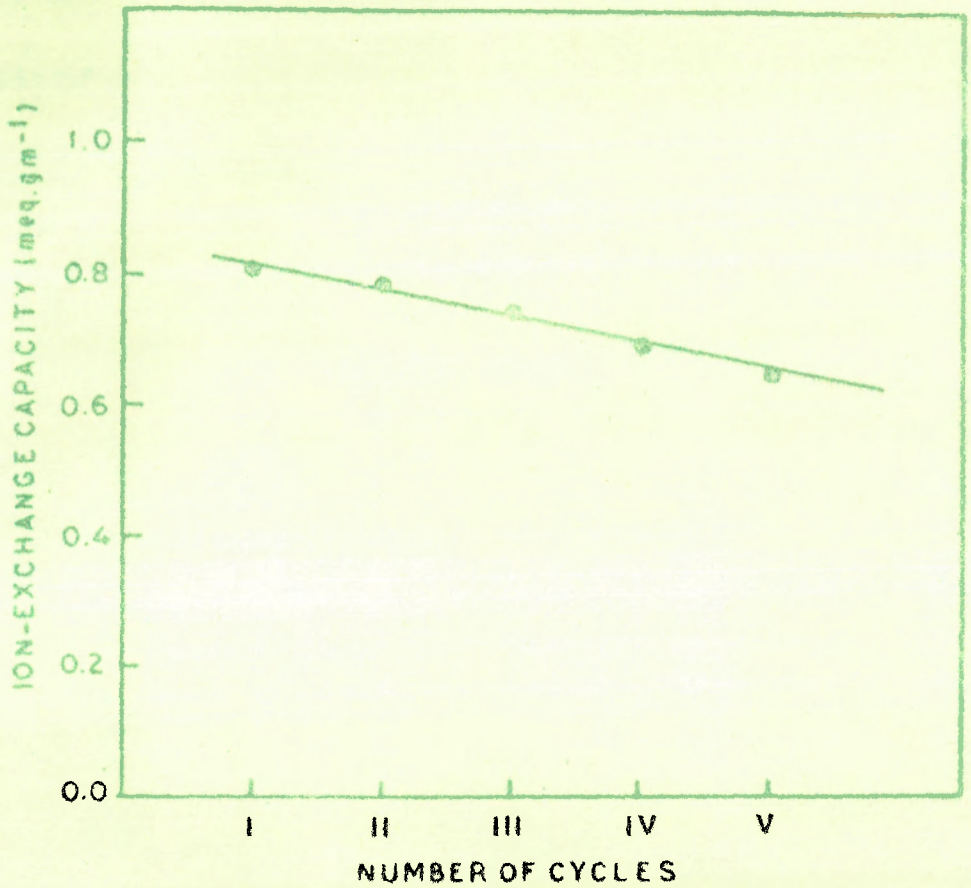


FIG. 18 PLOT OF ION-EXCHANGE CAPACITY AGAINST NUMBER OF REGENERATION CYCLES (FOR CHLORIDE IONS)

exchangers is dependant to some extent on the volume and concentration of eluent being weak cation or anion-exchanger. For determining the optimum conditions for the concentration of eluent 1 gm thorium triethanolamine in thiocyanate form was taken in the column. 0.01 M, 0.05 M, 0.1 M, 0.5 M, 1.0 M, 2.0 M, 3.0 M solutions of sodium nitrate were used as eluent. The eluted thiocyanate solution was titrated against 0.01 M silver nitrate solution. The volume of effluent in all of the cases was fixed as 300 ml. The results are shown in Table 13 and plotted in figure 19. Thiocyanate ion was chosen for the sake of smooth end point detection in titrations.

TABLE 13

ION-EXCHANGE CAPACITY OF ELUTING REAGENT AS A FUNCTION OF CONCENTRATION

Sl. No.	CONCENTRATION OF $NaNO_3$ (Molarity)	ION-EXCHANGE CAPACITY ($meq.gm^{-1}$)
1.	0.01	0.30
2.	0.05	0.40
3.	0.10	0.52
4.	0.50	0.58
5.	1.00	0.60
6.	1.50	0.61
7.	2.00	0.61
8.	3.00	0.61

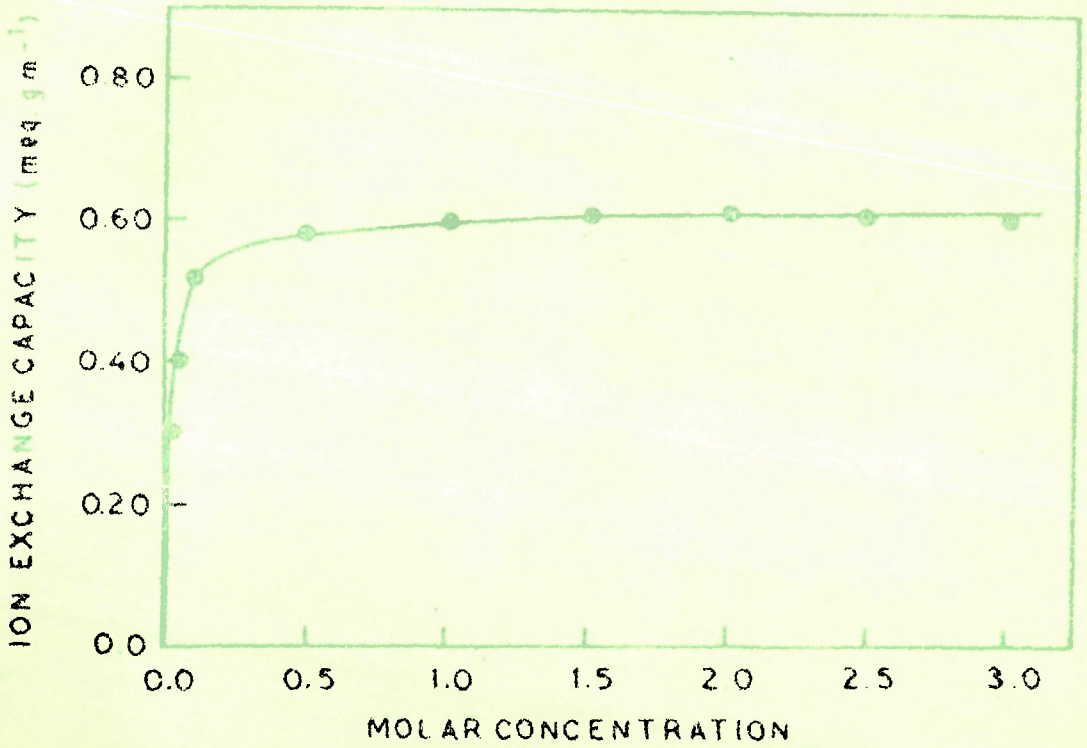


FIG. 19 ANION EXCHANGE CAPACITY AS A FUNCTION OF CONCENTRATION OF SODIUM NITRATE (FOR THIOCYANATE IONS)

Sorption Capacity

For determining the sorption capacity exchanger weighing one gm. was taken in the column. The exchanger was thoroughly washed with deionised water till excess of copper ions were removed. 0.5 N EDTA solution was used as an eluent. The effluents were collected in 10 ml fractions at a rate of 0.5 ml min^{-1}. For the determination of metal ions, the effluent in the fractions was treated with perchloric acid and nitric acid in the volume ratio of 2:1 to decompose the organic matter (EDTA). The solution was evaporated till a solid mass in the solution remained. This mass was dissolved with deionized water. Sodium acetate trihydrate was added to the beaker having the solution. For copper ions the solution was titrated against 0.01 N EDTA solution using buffer of pH 3.6 and PAN indicator. The sorption capacity of thorium was found to be 0.78 $meq.gm^{-1}$.

Chemical Stability

The chemical stability of thorium triethanolamine sample was determined by shaking 0.5 gm of exchanger for four hours in respective solutions in which its dissolution was to be checked. In the supernatant liquid the amount of thorium was determined by titrating against 0.02 N solution of EDTA while triethanol amine was determined spectrophotometrically by ninhydrin (14). The results are shown in Table 14.

TABLE 14

STABILITY OF THORIUM TRIETHANOLAMINE IN DIFFERENT MEDIA

Sl. No.	Solvent	Solubility (mg/50 ml)	
		Thorium	Triethanol amine
1.	Deionised water	00	00
2.	Nitric acid (0.10 N)	5.80	12
3.	Hydrochloric acid (0.10 N)	11.60	18
4.	Phosphoric acid (0.10 N)	00	00
5.	Sulphuric acid (0.10 N)	23.20	45
6.	Perchloric acid (0.10 N)	8.75	17.50
7.	Acetic acid (0.10 N)	1.40	3.50
8.	Formic acid (0.10 N)	0.09	1.50
9.	Ammonium hydroxide (1 N)	00	00
10.	Sodium hydroxide (1 N)	00	00
11.	Methyl alcohol	00	00
12.	Ethyl alcohol	00	00

Composition

500 mg of thorium triethanolamine was dissolved in 25 ml of aquaregia. It was diluted to 100 ml in a standard flask with

deionized water. The amount of thorium present in the solution was determined by chelometric titration using Cu-Pan indicator. Triethanolamine present in the other portion of the sample was determined spectrophotometrically by ninhydrin.

For the estimation of triethanolamine, a known amount of the sample was taken and mixed with 1:99 mixture of hydrochloric acid concentration and isopropanol so that the amine concentration is 2.20×10^{-4} m.moles/litre. To a 1 ml aliquot, 5 ml of pyridine and 2 ml of 0.2% ninhydrin solution in isopropanol were added. The solution was diluted to 10 ml with 1:99 hydrochloric acid, isopropanol mixture. It was then mixed and heated for 7 minutes at 75°C. The absorbance was read at 575 mμ. Thorium and triethanol amine were found to be in the mole ratio of 1:3.

Qualitative Tests

To check the presence of different constituents, the exchanger sample was subjected to a qualitative test for thorium (15), carbon and nitrogen (16). Thorium was detected by thorin. Nitrogen was detected with benzidine solution. For the test of carbon hundred milligram of silver arsenate were mixed in a micro test tube with the solid sample to be tested. The mixture was covered with an equal quantity of silver arsenate and heated for 1 hour over a microburner. After cooling a drop or two of the solution of phosphomolybdic acid is added. A blue

colour appears within 2 minutes. The intensity of the colour obtained depends on the quantity of oxidisable carbon in the sample.

Heat Treatment

Thorium triethanolamine sample was heated at different temperatures in a muffle furnace for 2 hours. The anion exchange capacity for thiocyanate ion was then determined by column operation method. The capacity at 40°C, 60°C, 100°C, 150°C, 200°C, 300°C was found to be 0.61, 0.60, 0.46, 0.38, 0.34, 0.30 respectively. The results are plotted in figure 20 and presented in Table 15.

TABLE 15

ANION-EXCHANGE CAPACITY OF THORIUM TRIETHANOLAMINE SAMPLES AT DIFFERENT DRYING TEMPERATURES FOR THIOCYANATE IONS

TEMPERATURE (°C)	CAPACITY ($meq.gm^{-1}$)
40	0.61
60	0.60
100	0.46
150	0.38
200	0.34
300	0.30

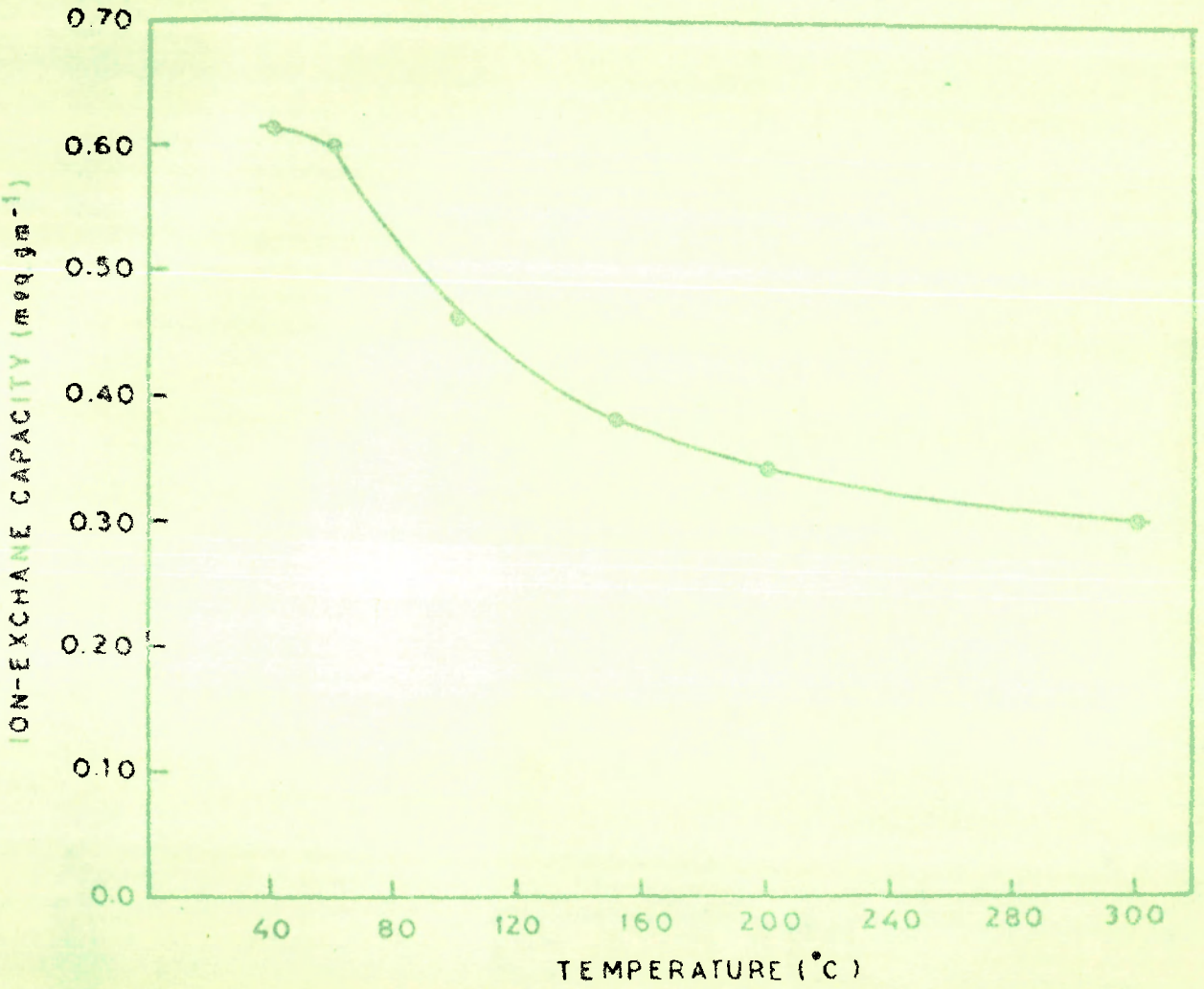


FIG. 20 ANION EXCHANGE CAPACITY OF THORIUM TRI-ETHANOLAMINE AT DIFFERENT DRYING TEMPERATURES

Structural Studies

For characterisation of the exchanger I.R. studies were performed. Infra red spectrum of thorium triethanol-amine sample was obtained by using KBr disc. The results are presented in figure 21.

Breakthrough Capacity

The breakthrough capacity was determined by column operation. Solutions of copper nitrate containing 12.60 mg/10 ml was passed through a column loaded with 1 gm of thorium triethanol amine on its glass wool support. The flow rate was adjusted to 0.5 ml min^{-1}. The amount of copper(II) collected in each 10 ml fraction was determined. The results are summarized in Table 16 and plotted in figure 22.

Potentiometric titrations

pH titrations of thorium triethanol-amine were performed by shaking 0.5 gm of exchanger with solution of hydrochloric acid, sulphuric acid and nitric acid with their respective salts by Topp and Pepper method (17). For these titrations 0.1 N acid solutions and 0.1 N salt solutions were taken in such a way that the total volume remained 50 ml in each case. 0.5 gm of thorium triethanol-amine was added in each conical flask containing the reaction mixture. The pH of the solution after shaking for 4 hours was noted. The results are plotted in figure 23.

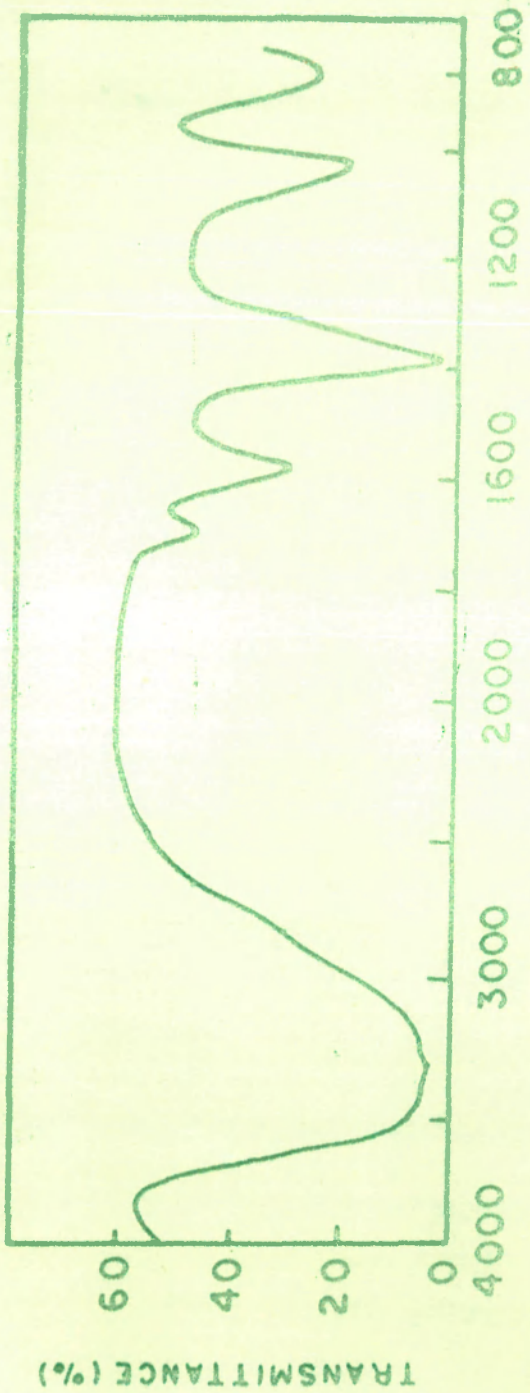


FIG. 21 I.R. SPECTRUM OF THORIUM TRIETHANOLAMINE

TABLE 16

BREAKTHROUGH CAPACITY OF THORIUM TRIETHANOLAMINE

Concentration of feed solution = 12.60 mg

Flow rate = 0.5 ml min^{-1}

FRACTIONS (ml)	COPPER(II) IN EFFLUENT
20	00
40	00
60	2.00
80	5.40
100	8.45
120	10.00
140	11.00
160	11.50
180	12.00
200	12.20
220	12.20
240	12.20
260	12.20

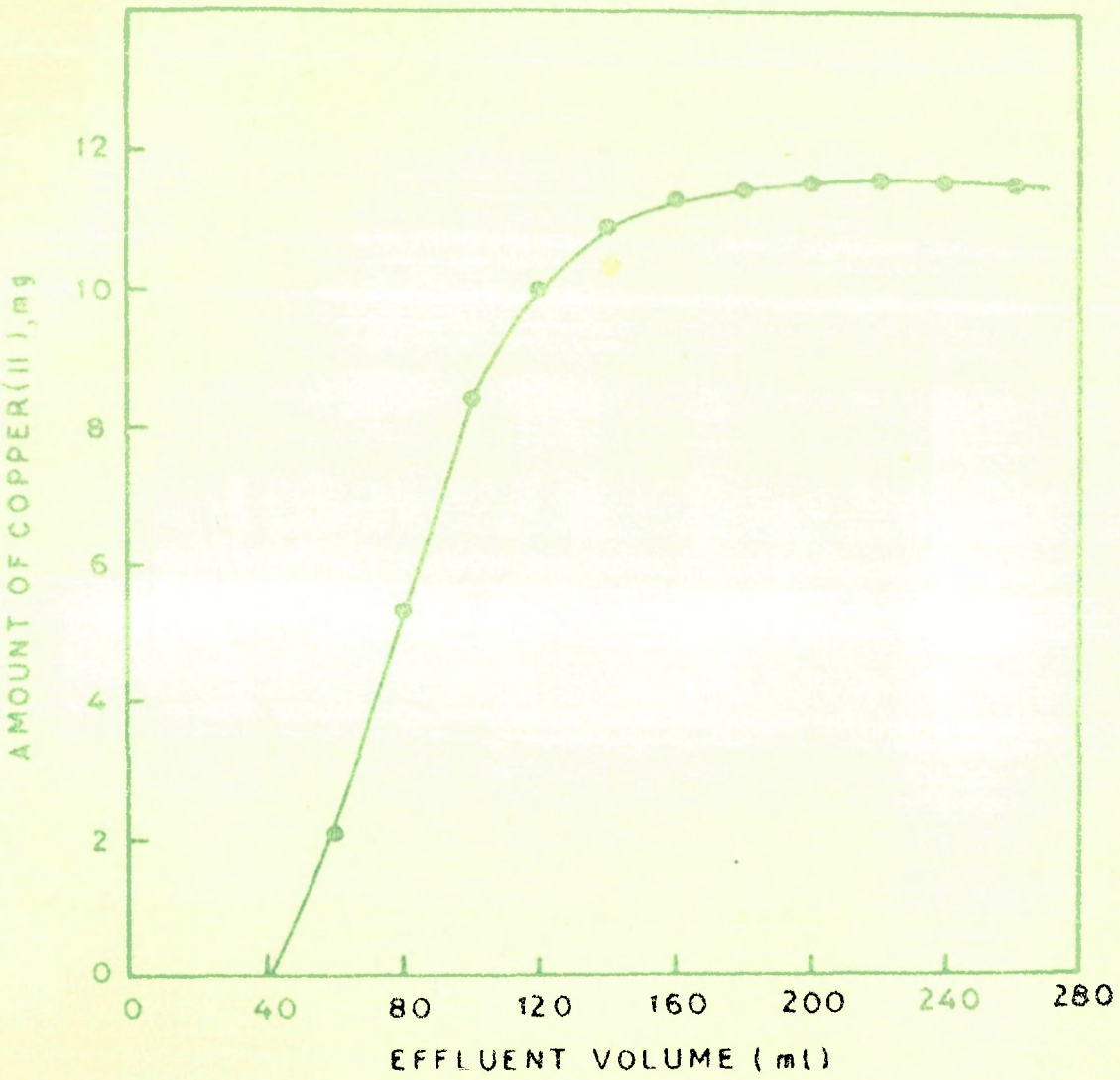


FIG. 22 BREAK THROUGH CURVE

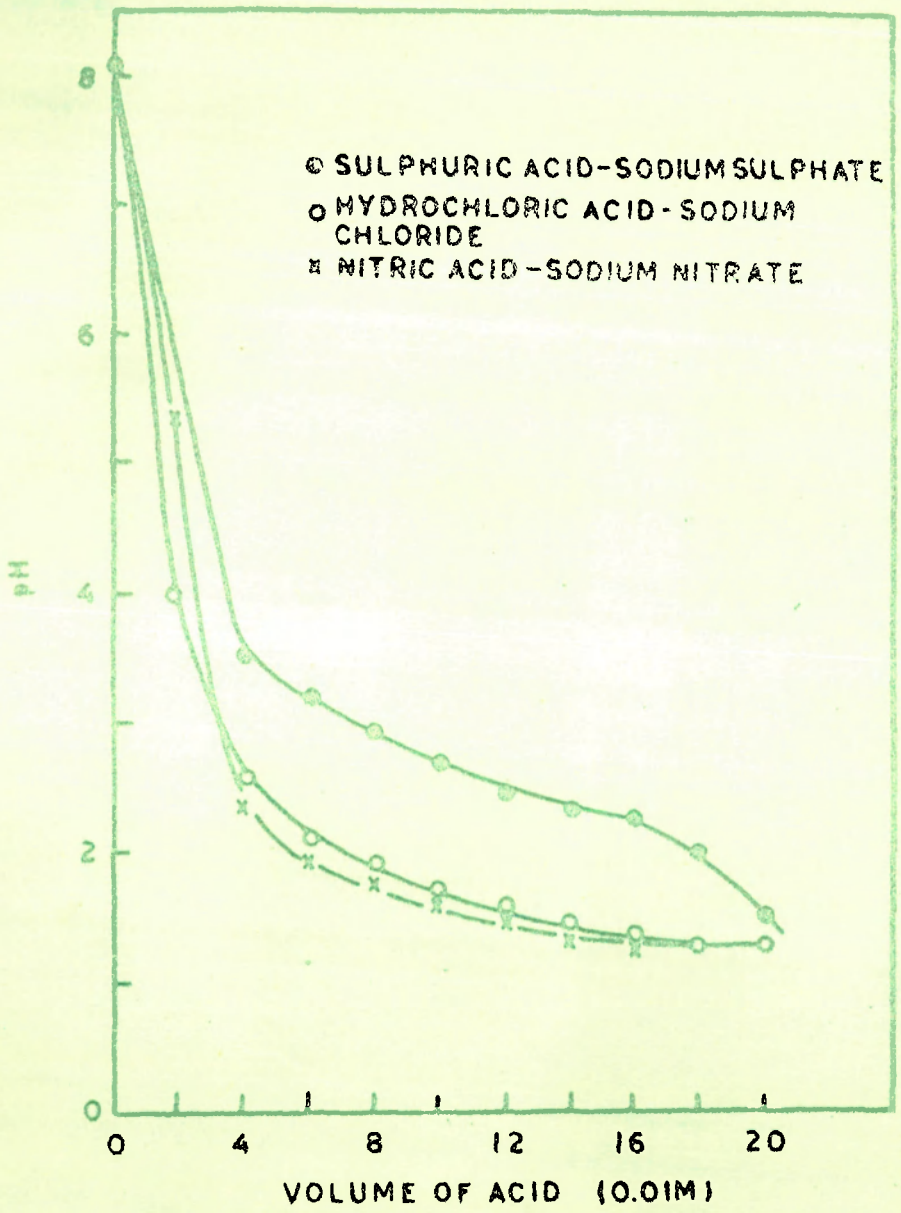


FIG. 23 PH TITRATION CURVES OF THORIUM-TRIETHANOLAMINE

Distribution Coefficients

The distribution studies for anions and cations were carried out by batch process. 1 ml of anionic or cationic solution was mixed with the solution in which the distribution studies of the exchanger were to be determined. The final volume was kept 50 ml in all cases. This solution was shaken with 0.5 gm of exchanger in a 250 ml conical flask for 4 hours. The supernatant liquid was drained off and the amounts of anions or cations remaining in the solution were determined titrimetrically. The K_d values were then determined by using the formula

$$K_d = \frac{I-F}{F} \times \frac{50}{0.5} \text{ ml } g^{-1}$$

where I and F are the volume of titrant before and after the equilibrium. The K_d values for anions in deionized water and different molar solutions of NH_4OH are reported in Table 17.

TABLE 17

DISTRIBUTION COEFFICIENTS FOR ANIONS ON THORIUM TRIETHANOLAMINE

SAMPLE NO.	ANIONS	K_d ml gm^{-1}				
		D.M.W.	0.001 N NH_4OH	0.01 N NH_4OH	0.10 N NH_4OH	0.50 N NH_4OH
1	Chloride	290	250	70	10	05
2	Bromide	220	220	70	06	03
3	Iodide	200	151	66	17	05
4	Thiocyanate	304	304	98	16	06
5	Thiosulphate	2180	2180	307	86	01
6	Dichromate	3400	950	62	36	08
7	Sulphate	T.A.	T.A.	340	169	35
8	Persulphate	2375	2375	800	200	266
9	Iodate	5140	870	106	48	21
10	Arsenate	1820	581	250	60	54
11	Bromate	1066	1066	220	15	01
12	Chromate	T.A.	1900	900	280	15
13	Ferricyanide	290	279	121	90	70
14	Vanadate	297	185	185	81	81
15	Ferrocyanide	512	512	57	10	03
16	Sulphite	175	175	155	51	15
17	Sulphate	450	266	266	95	50
18	Oxalate	485	485	225	80	56
19	Molybdate	300	300	120	50	15
20	Hypochlorite	500	100	100	71	50
21	Tungstate	500	500	200	150	72

T.A. = Total Adsorption

TABLE 18

DISTRIBUTION COEFFICIENTS FOR CATIONS ON THORIUM TRIETHANOLAMINE

SAMPLE NO.	CATIONS	K_d ml gm^{-1}				
		D.M.W.	0.001 M EDTA	0.005 M EDTA	0.01 M EDTA	0.05 M EDTA
1	Cu^{2+}	175	83	35	00	00
2	Ni^{2+}	00	00	61	25	00
3	Co^{2+}	100	62	30	20	00
4	Mg^{2+}	00	00	00	00	00
5	Fe^{2+}	400	400	67	10	00
6	Hg^{2+}	85	85	85	10	00
7	Ba^{2+}	00	00	00	00	00
8	Sr^{2+}	00	00	00	00	00
9	Fe^{3+}	816	19	05	00	00
10	UO_2^{+}	100	15	15	00	00
11	Ca^{2+}	00	00	00	00	00
12	V^{4+}	33	33	09	00	00
13	Ce^{4+}	33	15	08	00	00
14	La^{3+}	34	14	08	00	00
15	Y^{3+}	100	20	00	00	00
16	Cd^{2+}	42	29	11	00	00
17	Bi^{2+}	70	29	10	00	00
18	Zn^{2+}	37	32	25	10	00

Separations

On the basis of large differences in distribution coefficient values, a number of separations were tried. 2 gm of thorium triethanolamine in nitrate form was taken in a glass column having a height 30 cms and diameter 0.69 cm. The mixture containing known amounts of anions to be separated was transferred onto the column. The solution was repeatedly passed through the column at a very slow flow rate to allow complete adsorption of the anions. 10 ml fractions of the eluate were collected at a flow rate 0.5 ml min^{-1}. The amount of anions present in each fraction was then determined by standard methods. The same procedure was applied for the separation of cations. The eluted fraction contained only one component of the mixture. The separations of $Cr_2O_7^{2-}$ from Br^-, CrO_4^{2-} from Br^-, SO_4^{2-} from I^-, SrO_3^{2-} from Br^-, SO_4^{2-} from Br^-, CrO_4^{2-} from I^-, $Cr_2O_7^{2-}$ from I^- and separations of Cu(II) from Mg(II), Co(II) from Mg(II), Cu(II) from Sr(II), Pb from Ba(II), Pb(II) from Mg(II) and Pb(II) from Sr(II) were achieved. The order of elution and elution curves are shown in figures 24a-27 and 28a-30b and the separations of anions and cations are given in Tables 19 and 20 respectively.

Rate

The rate was determined by batch process. 0.20 milli-equivalents of thiocyanate was shaken with 0.5 gm of thorium triethanolamine at different intervals of time. The amount of thiocyanate remaining in the solution was then determined. The results are given in Table 21 and plotted in figure 31.

TABLE 19

SEPARATIONS OF ANIONS ON THORIUM TRIETHANOLAMINE COLUMN

SL. NO.	MIXTURE	ELUENT	ELUATE (ml)	AMOUNT LOADED (mg)	AMOUNT FOUND (mg)	% ERROR
1.	CrO_4^{2-}	0.10 M NH_4OH	100	7.70	6.90	2.40
	Br^-	0.01 M NH_4OH	90	3.01	2.94	2.32
2.	$Cr_2O_7^{2-}$	0.10 M NH_4OH	100	4.68	4.57	2.35
	Br^-	0.01 M NH_4OH	90	3.01	2.97	1.32
3.	SO_4^{2-}	0.10 M NH_4OH	90	1.35	1.30	2.25
	I^-	0.01 M NH_4OH	90	2.90	2.82	2.75
4.	$S_2O_3^{2-}$	0.10 M NH_4OH	110	5.39	5.35	0.74
	Br^-	0.01 M NH_4OH	90	3.01	2.97	0.99
5.	SO_4^{2-}	0.10 M NH_4OH	70	1.34	1.30	2.98
	Br^-	0.01 M NH_4OH	90	3.01	2.94	1.99
6.	$Cr_2O_7^{2-}$	0.10 M NH_4OH	100	4.69	4.61	1.70
	I^-	0.01 M NH_4OH	90	2.90	2.86	1.37
7.	CrO_4^{2-}	0.10 M NH_4OH	110	7.07	6.99	1.13
	I^-	0.01 M NH_4OH	90	2.90	2.82	2.75

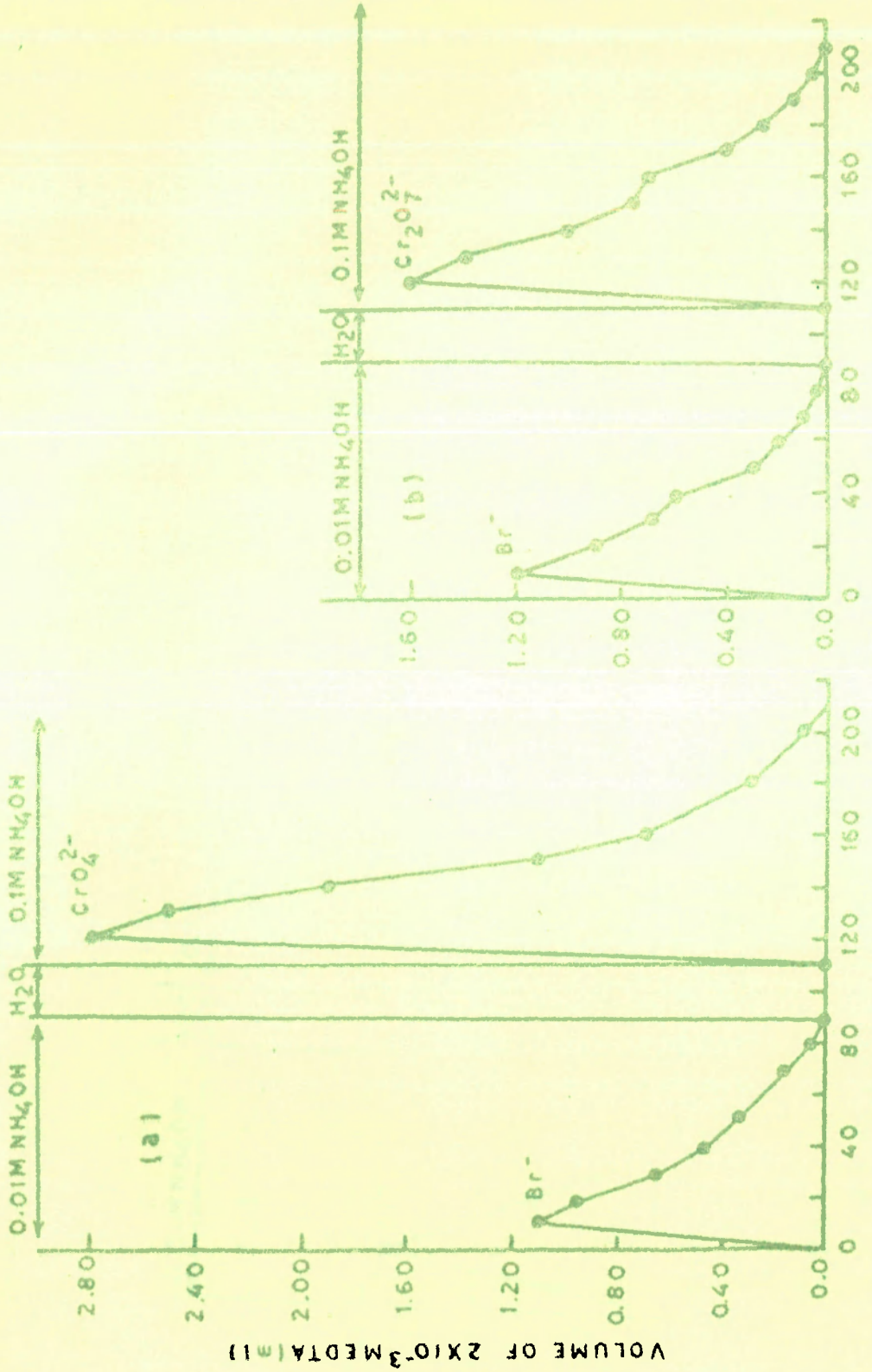


FIG. 24
(a) SEPARATION OF Br^- – CrO_4^{2-}
(b) SEPARATION OF Br^- – $Cr_2O_7^{2-}$

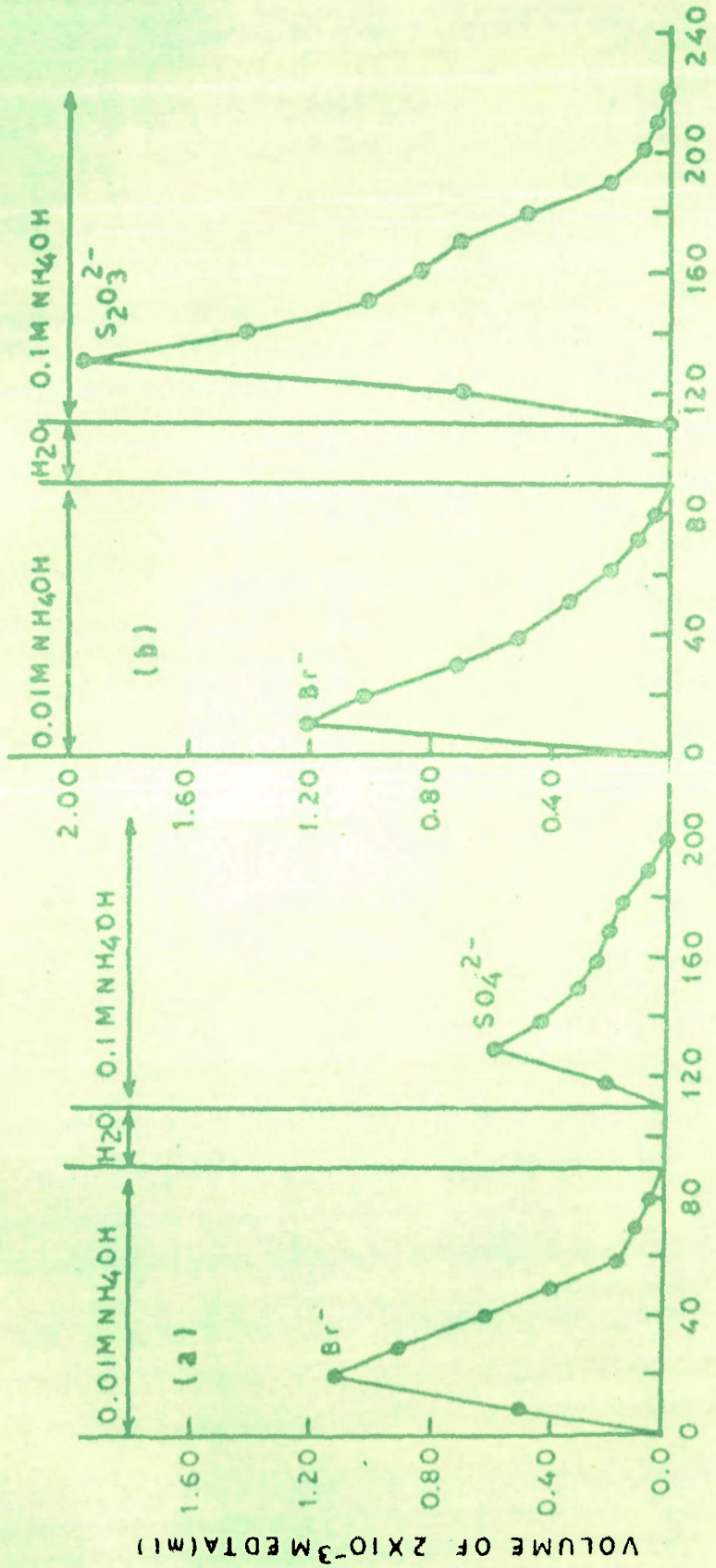


FIG. 25
(a) SEPARATION OF Br^- – SO_4^{2-}
(b) SEPARATION OF Br^- – $S_2O_3^{2-}$

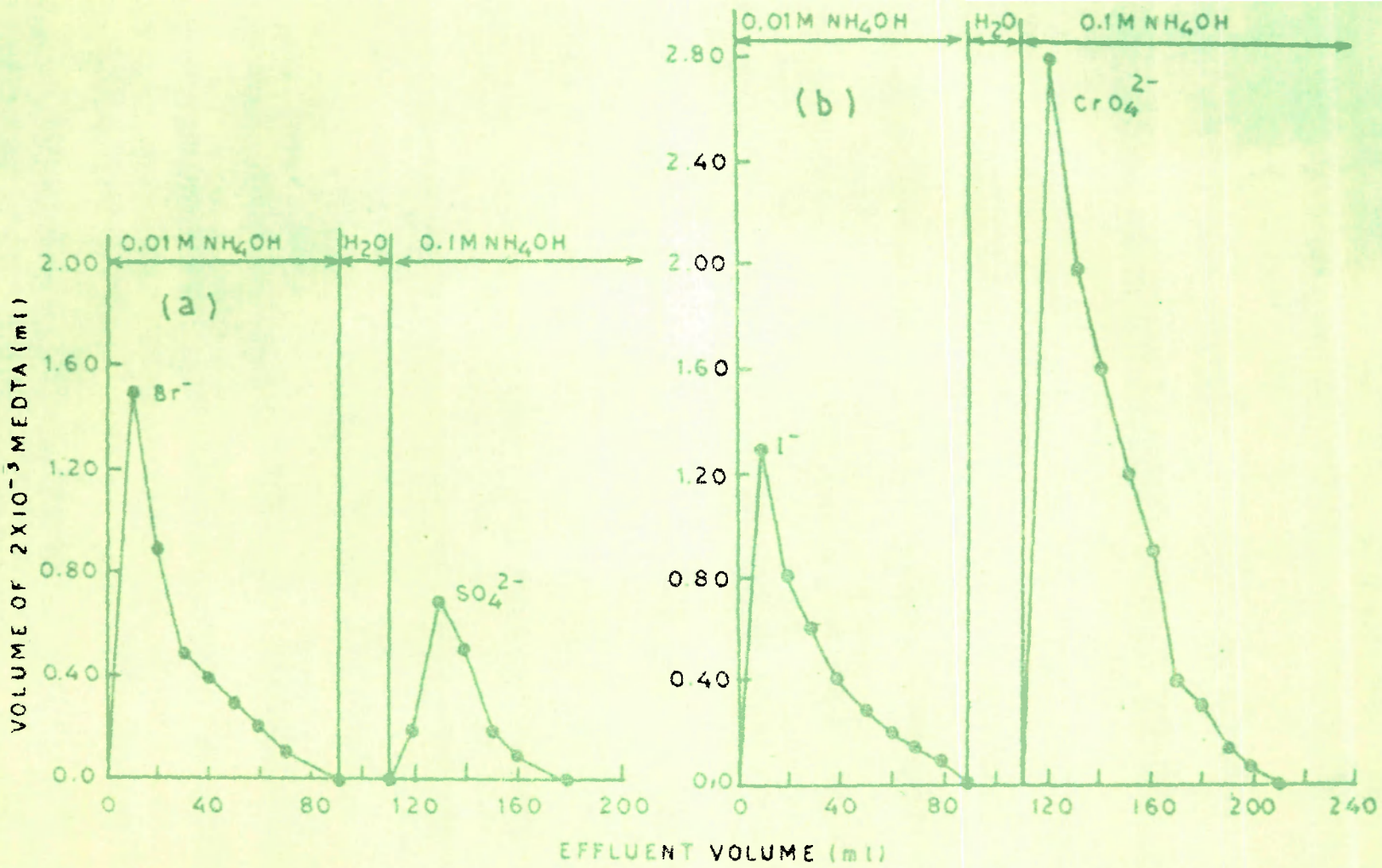


FIG. 26

(a) SEPARATION OF $Br^- - SO_4^{2-}$

(b) SEPARATION OF $I^- - CrO_4^{2-}$

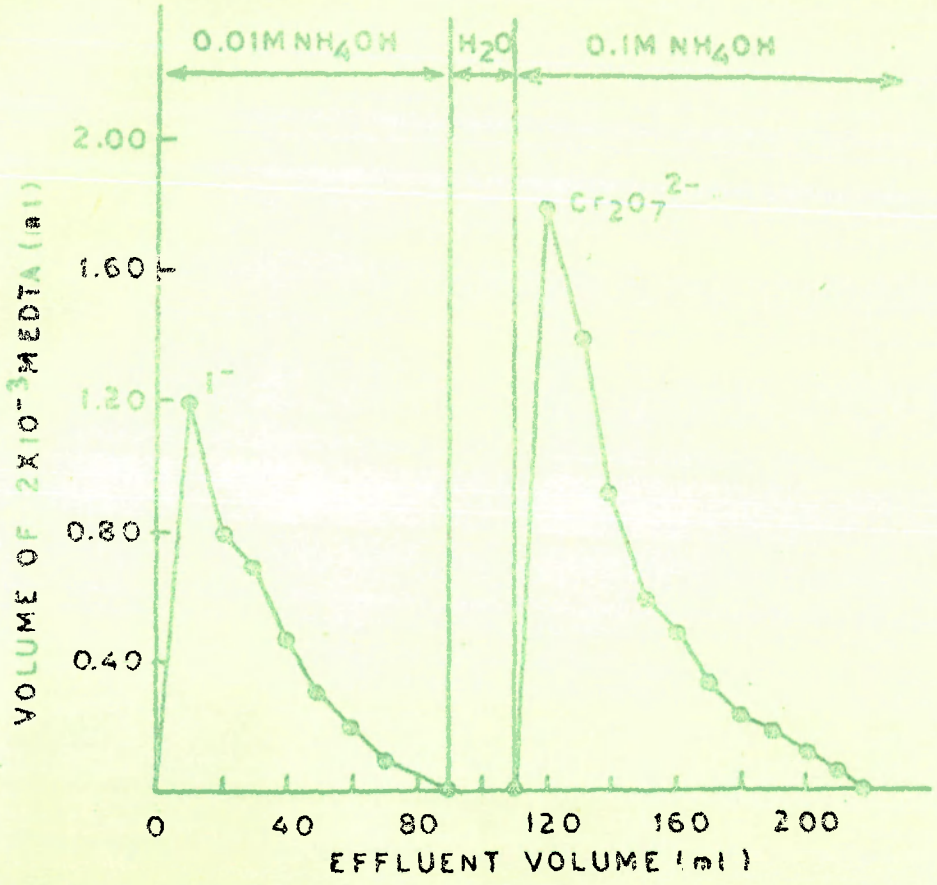
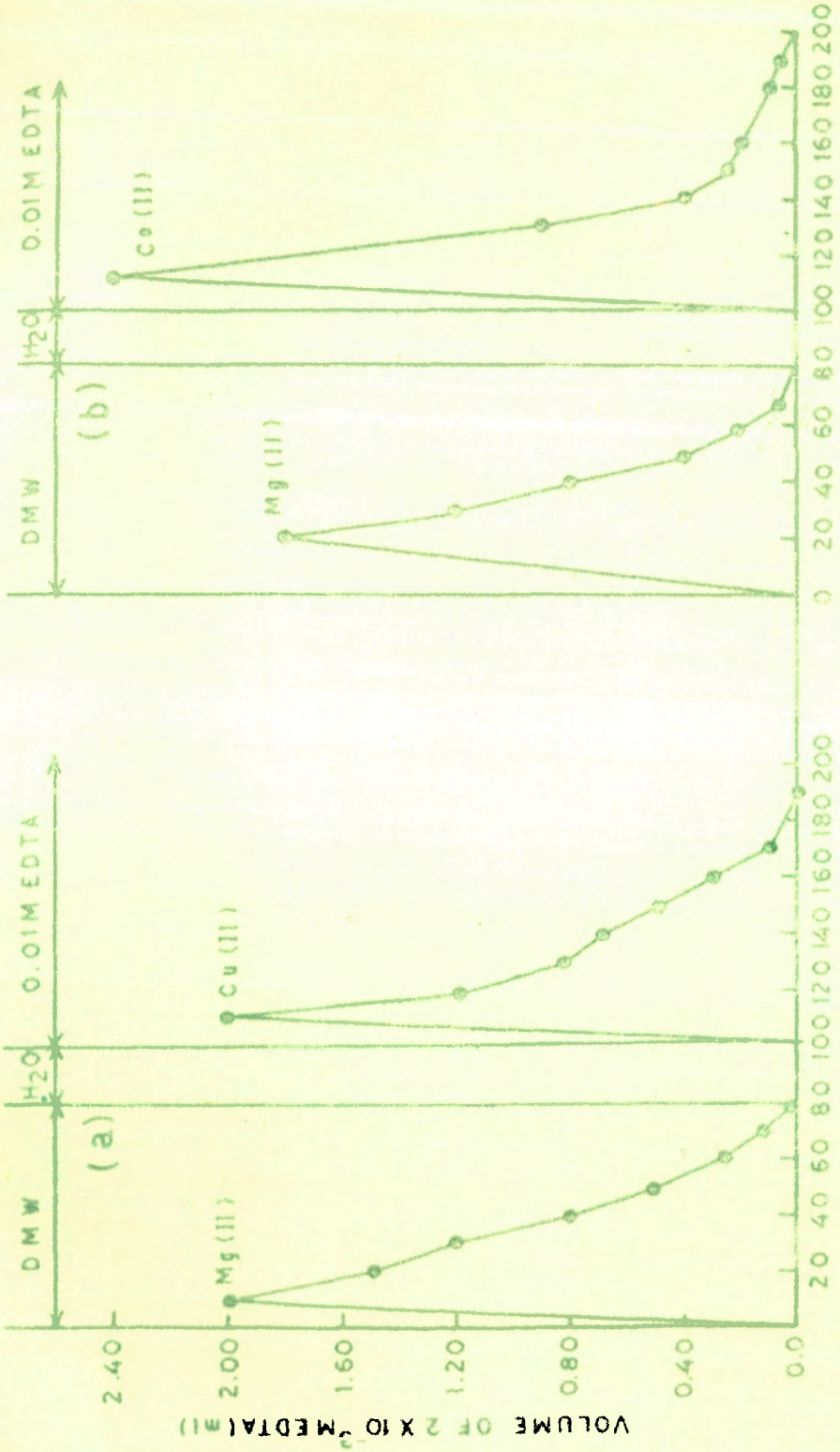


FIG. 27 SEPARATION OF $I^- - Cr_2O_7^{2-}$

TABLE 20

SEPARATIONS OF CATIONS ON THORIUM TRIETHANOLAMINE COLUMN

SL. NO.	MIXTURE	ELUENT	ELUATE (ml)	AMOUNT LOADED (mg)	AMOUNT FOUND (mg)	% ERROR
1.	Cu(II)	0.01 M EDTA	90	0.70	0.68	2.80
	Mg(II)	Deionised water	80	0.31	0.30	3.20
2.	Co(II)	0.01 M EDTA	100	0.77	0.76	1.30
	Mg(II)	Deionised water	80	0.31	0.30	3.20
3.	Pb(II)	0.01 M EDTA	90	2.07	2.04	1.40
	Ba(II)	Deionised water	110	0.66	0.65	1.50
4.	Cu(II)	0.01 M EDTA	100	0.70	0.69	1.40
	Sr(II)	Deionised water	100	1.31	1.30	0.76
5.	Pb(II)	0.01 M EDTA	90	2.07	2.02	2.40
	Mg(II)	Deionised water	90	0.31	0.30	3.20
6.	Pb(II)	0.01 M EDTA	90	2.07	2.04	1.40
	Sr(II)	Deionised water	100	1.31	1.30	0.76



F.G.28

(a) SEPARATION OF Cu (II) - Mg (II)
(b) SEPARATION OF Mg (II) - Co (II)

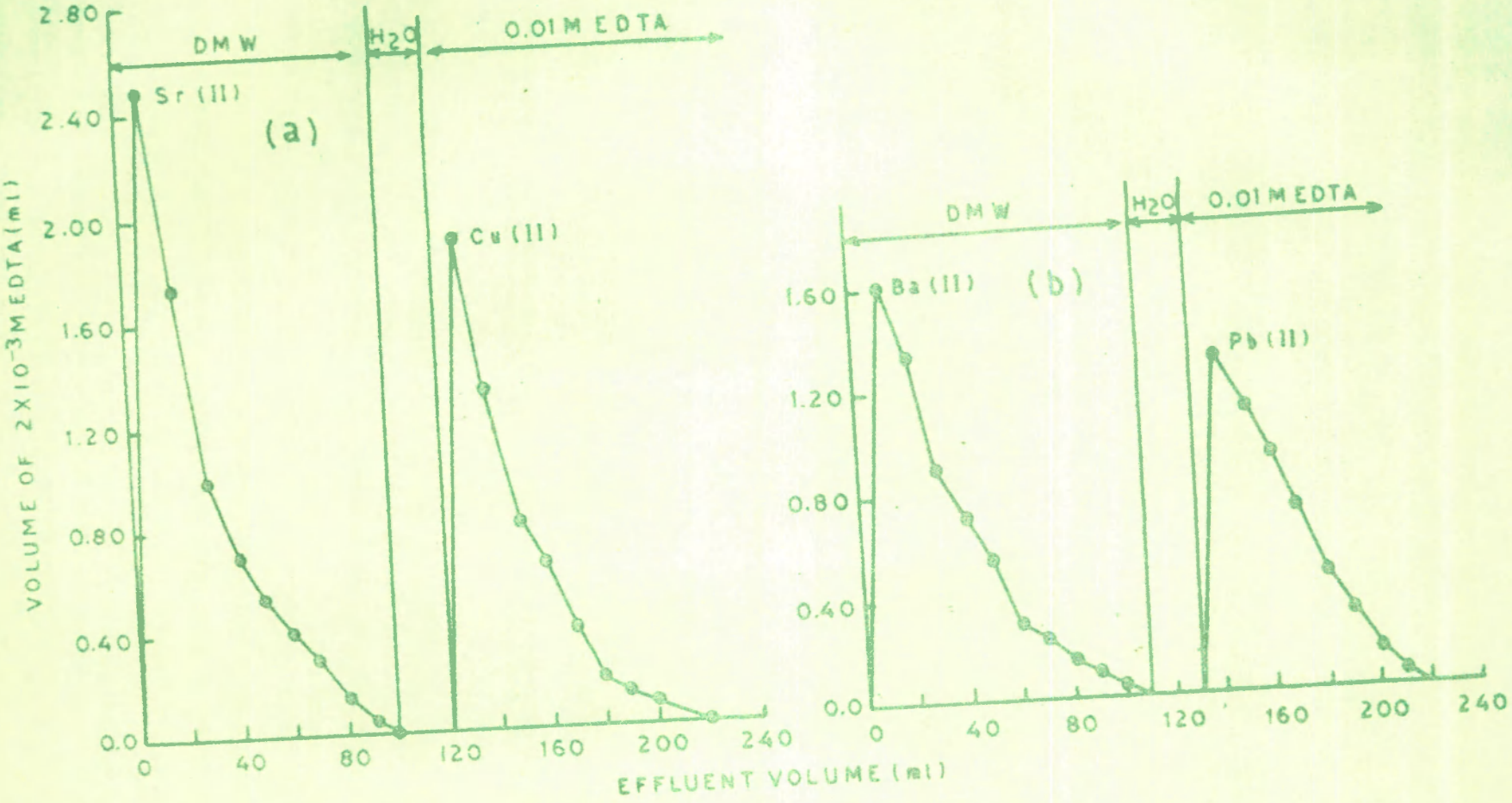


FIG. 29

(a) SEPARATION OF Sr(II) - Cu (II)

(b) SEPARATION OF Ba(II) - Pb(II)

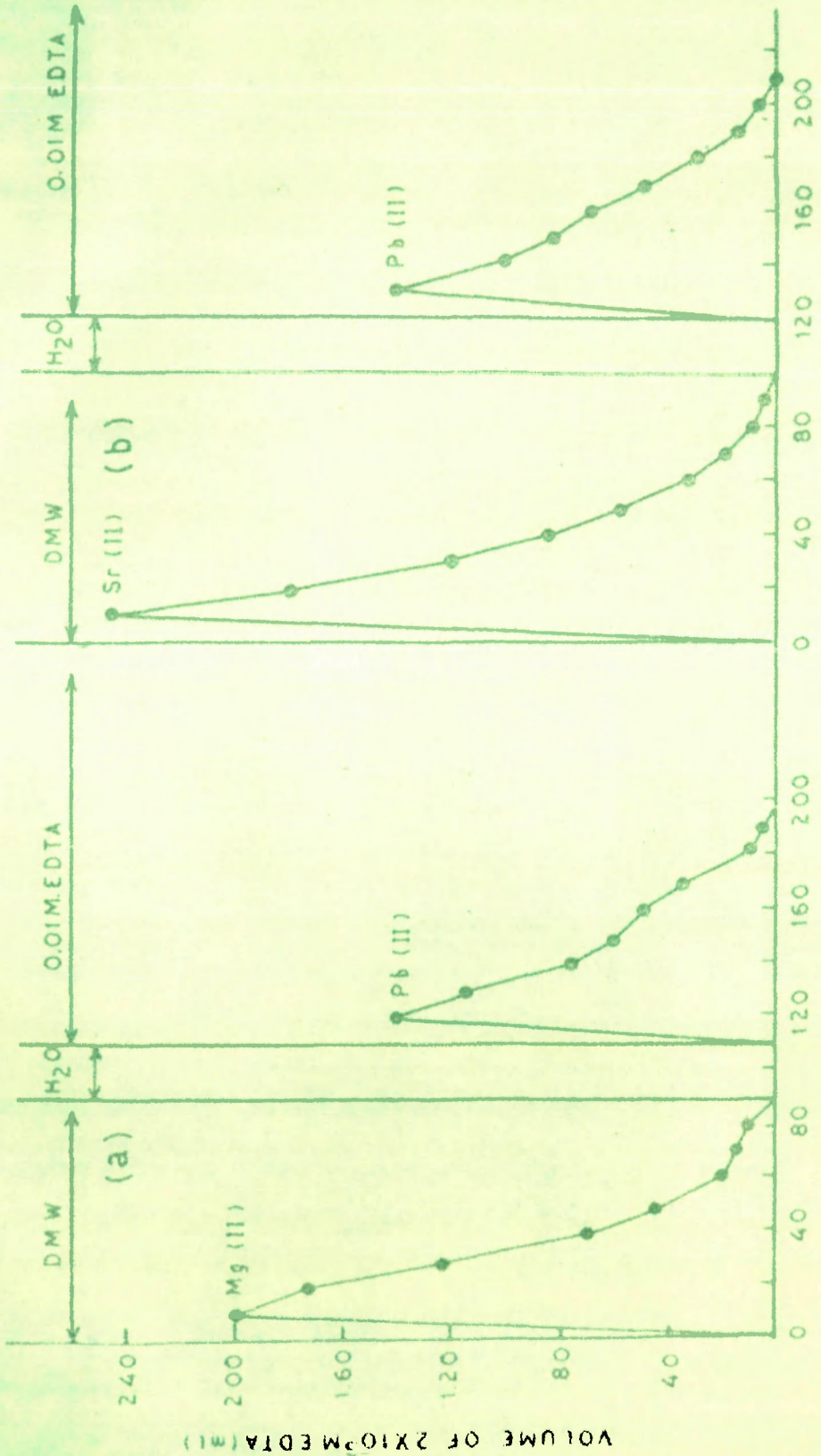


FIG. 30

(a) SEPARATION OF Mg (II) – Pb (II)
(b) SEPARATION OF Sr (II) – Pb (II)

TABLE 21

RATE OF ADSORPTION OF THIOCYANATE IONS

TIME (minutes)	INITIAL AMOUNT OF SCN^- (m.moles)	AMOUNT OF SCN^- ADSORBED (m.moles)
00	0.20	00
05	0.20	0.07
10	0.20	0.09
15	0.20	0.10
20	0.20	0.11
40	0.20	0.14
60	0.20	0.15
100	0.20	0.15
120	0.20	0.15

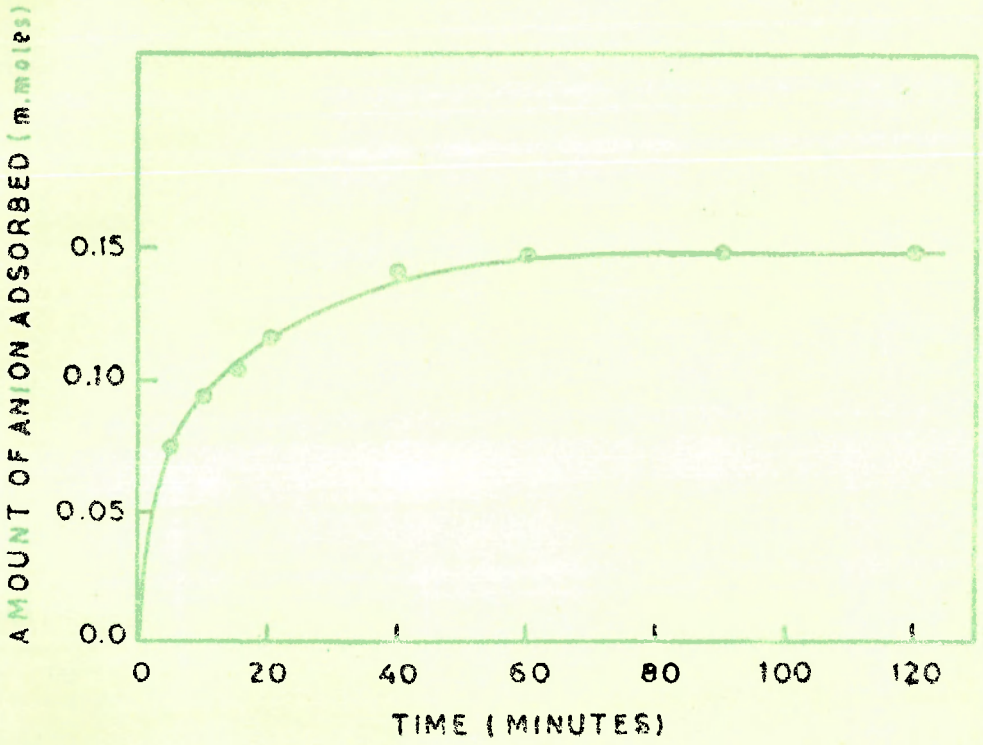


FIG. 31 RATE OF ADSORPTION OF THIOCYANATE IONS

DISCUSSION

It is clear from Table 11 that for the precipitation to occur metal to amine ratio must be 1:4. Any alteration in the ratio of metal to amine ratio resulted either in mild precipitation or in disappearance of the precipitate.

It can be seen from Table 12 that the material possesses a good anion-exchange capacity and ranges from 0.90 to 0.18. It is, therefore, likely that the incorporated triethanolamine group acquires a free charge on its nitrogen atom and is responsible for the anion-exchange behaviour of the material.

It is worthmentioning that thorium triethanolamine does not show any cation exchange capacity. When thorium triethanolamine in H^+ form was kept in contact with a solution of sodium nitrate, no release of H^+ was observed. Similar experiment with thorium triethanolamine in copper form when eluted with sodium nitrate failed to show any liberation of Cu(II). However, the exchanger possesses appreciable sorption capacity. Metal ions were taken up by the exchanger and the elution took with EDTA solutions. The inability of thorium triethanolamine to show any hydrogen liberation capacity may be related to the possibility that there is no fixed negative charge with the exchanger matrix. The sorption of the metal ions took place due to the presence of nitrogen atom of amine group that offers sites for the chelation with the metal ions. As the stability of metal-EDTA is higher than other metal-ligand complexes, the treatment of

the metal exchanger with EDTA detaches metal from the exchanger. Thus eluate is having metal-EDTA complex. Sorption capacity was found to be 0.78 m.moles gm^{-1}. The exchanger acquired the colour of sorbed metal ions which can be conspic ously seen. The visible colour change due to the sorption of different metal ions is shown in Table 22.

TABLE 22

COLOUR CHANGE DUE TO SORPTION

SL. NO.	METAL IONS SORBED	COLOUR OF THE EXCHANGER
1.	Copper(II)	Blue
2.	Iron(III)	Brown
3.	Nickel(II)	Green
4.	Zinc(II)	No change
5.	Cobalt(II)	Pink
6.	Mercury(II)	No change
7.	Lead(II)	No change
8.	Magnesium(II)	No change
9.	Manganese(II)	Light brown
10.	Strontium(II)	No change

Figure 18 shows the regeneration cycle which was studied upto five cycles. The determination of the capacity after recycling showed slight loss in capacity. This suggests that the same column of ion-exchanger may be used again and again.

Ion-exchange capacity of inorganic ion-exchangers depend to some extent on the volume and concentration of the eluent. So the concentration curve is essential for characterizing an ion-exchanger. It is clear from Table 13 that the suitable concentration for a fixed volume 300 ml of the eluent sodium nitrate is 1.0 M for thorium triethanolamine.

The results of chemical stability of thorium triethanol amine given in Table 14 indicate that the exchanger is quite stable in organic and neutral aqueous solutions. The material shows dissolution in strong acidic media, hence should be avoided. Sodium hydroxide ammonium hydroxide having 1 M concentration can, however, be safely used.

The results of drying temperatures of thorium triethanol amine shown in Table 15 indicate that the capacity decreases with the increase in drying temperature. Hence the material thorium triethanolamine must be used as an anion exchanger at temperatures below 100°C.

The infrared absorption spectrum of thorium triethanol

amine in figure 21 shows the following absorption peaks.

1. A broad peak ranging from 3300-3500 cm^{-1} is attributed to the -OH stretching vibrations.
2. A weak peak between 1770-1780 cm^{-1} is due to C-O stretching vibration.
3. C-C stretching vibration is observed in the frequency range 1600-1620 cm^{-1}.
4. C-N bending frequency is due to the frequency range in 1020-1220 cm^{-1}.
5. A strong peak in the frequency range 1370-1490 cm^{-1} is observed due to C-H bending.
6. A peak at 850 cm^{-1} is because of the presence of thorium metal-oxygen bonding.

From the above observations it is clear that the exchanger still retains the amine group. The results of chemical analysis show the ratio of thorium and triethanol amine as 1:3.

Ion-exchange potentiometric titrations were performed with hydrochloric, nitric & sulphuric acid with their respective salts. It is clear from figure 23 that thorium triethanolamine in hydroxyl form behaves as monofunctional anion-exchanger.

The analytical utility of thorium triethanolamine can be observed from its amphoteric behaviour. The distribution behaviour of different anions are generally high. K_d values were appreciably lowered when a solution of NH_4OH was used for

equilibrium studies. A decrease in K_d values with the increase in the concentration of ammonium hydroxide is observed. When exchanger was placed in 0.1 M sodium hydroxide, the ion-exchange material showed high affinity for hydroxyl groups. Hence in the presence of hydroxyl group other ions showed little uptake.

On the basis of large differences in K_d values of various anions in different solvent systems, many separations were tried and achieved. CrO_4^{2-} from Br^-, $Cr_2O_7^{2-}$ from Br^-, SO_4^{2-} from I^-, $S_2O_3^{2-}$ from Br^-, SO_4^{2-} from Br^-, $Cr_2O_7^{2-}$ from I^- and CrO_4^{2-} from I^- were separated successfully and are presented in Table 19.

The distribution coefficients for cations are listed in Table 18. For some cations K_d values are high while for the other cations, the distribution coefficients are very low. K_d values were high in deionized water. The distribution behaviour of cations decreased as the concentration of EDTA solution was increased. Owing to the large differences in K_d values of different cations, many separations were achieved. Those practically achieved were of Cu(II), Co(II) and Pb(II) from Mg(II), Ba(II) and Sr(II) from Pb(II) and Cu(II) from Sr(II). The separations shown in Table 20 are quantitative and the error is within admissible error range. The order of elution and eluents used are shown in figures 24a-27 and 28a-30b.

The equilibrium studies plotted in figure 31 reveal that the equilibrium is attained within 30 minutes. Normally

the fast equilibration rate is not expected from inorganic ion exchangers. Presence of a chelation group (amine group) in thorium triethanolamine is possibly responsible for such a fast equilibration rate. This is an advantage of thorium triethanol amine over the polybasic acid type of inorganic ion-exchangers. The equilibration studies, however, were made by shaking the ion-exchange material with a particular anion solution for 4 hours to ensure complete equilibrium.

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C H A P T E R - V

SENSITIVE AND SELECTIVE ION-EXCHANGE COMBINED A.A.S. DETERMINATION OF TRACE ELEMENTS IN ROCKS

Rocks are of considerable importance in the earth sciences. Inspite of their geological significance their chemical analyses have little reference materials required for the standardization of instrumental techniques. Therefore, the analysis of the rocks may be taken as an important type of applied analysis.

The elements found in rocks may be divided into three groups from the analytical standpoint. The first group includes the major constituents, the second group comprises minor constituents and the third group includes the trace constituents. Trace element analysis in rock samples (silicate and sedimentary rocks) is considered important because it helps (i) in determining the origin and history of the rock, (ii) in finding out the source of trace elements, (iii) in detecting the elements hazardous to health (Hg,Ba), (iv) in complete analysis of rocks, and (v) in the extraction of elements of economic importance from the rock samples.

Modern analytical techniques like atomic absorption spectroscopy, flame emission spectroscopy, x-ray fluorescence and neutron activation analysis (1-4) have been applied for their direct determination. There is necessity for modification which are being developed to take care of interferences. High calcium concentration present in the rocks causes interferences in the determination of Ba by A.A.S. Calcium hydroxide formed in the flame has an emission band with a maximum at 554 nm overlapping

the analytical line at 553.4 nm. Lanthanum too interferes in the determination of barium due to the presence of La O which gives an absorption band at 553.6 nm. Aluminium interferes in the determination of alkaline earth metals (5). Magnesium oxide causes interferences because it gives band at 535.5 nm (6). Silicon interferes when in the form of sodium silicate but this interference is due to sodium. Alkali metals also reduce the ionisation of barium atoms. Fe, Ti and Li are highly interfering agents (7-10). Mn and Zn suffer from matrix interference (8). Hence it is necessary to separate these elements from the silicate matrix. The development of analytical schemes to include as many major, minor and trace elements as possible is important if it is desired to use only one or two portions of the sample. Separation schemes have been investigated and the results have been examined in detail by Strelow in a review (11). Such interferences cause low accuracy and low precision in these determinations (12). The accuracy, precision and possibility of removing interferences can be increased by a prior ion-exchange separation.

Ion-exchange chromatography gives quantitative separations of a large number of ions and it may be applied to rock analysis (13). Barium has been determined in trace amounts in silicates and minerals by ion-exchange chromatography and atomic absorption spectroscopy.

It is very important to develop standardised analytical methods which give selective separations and then the quantitative determination of the elements in individual solutions. After an ion-exchange separation, the analysis are carried out by atomic absorption spectrometry. The separation scheme is given to eliminate interferences of other ions for the determination of ion of interest. A scheme of ion-exchange separation of 15 elements and determination by A.A.S. has been applied to rock analysis (14). Govindaraju (15) has given a method of silicate analysis. By using ion-exchange dissolution and emission spectrometry, 13 elements were accurately determined. Szlaurova et al. (16) have proposed an analytical scheme for fifteen radionuclides by using seven cation and anion-exchangers.

In the present work the use has been made of the principles of classical wet analysis to investigate the presence and quantitative determination of trace elements in rock samples by converting an anion-exchange resin in the respective ionic forms to give the insoluble salts by the action of counter ion (an anion of the resin and the metal ion in the solution. The metal ions are then eluted by suitable eluting reagents forming soluble salt

EXPERIMENTAL

Reagents

All reagents used were of analytical reagent grade.

Amberlite IR-400 with 200-400 mesh size.

Apparatus

Atomic absorption spectrometer, S.P. 2900 (Philips).

Ion-Exchange

Amberlite IR-400 with 200-400 mesh was used. Ion-exchanger was taken in a column filled with glass wool support. The anion-exchanger was first converted into chloride form and then in suitable ionic forms as desired, by the respective salt solutions.

Analytical Procedure

Standard solutions of different metal ions were prepared by titration against EDTA solution. Separation of different metal ions was based on the ability of metal ions to form precipitate with particular anions. The columns of anion-exchangers were used by taking approximately 5 gm of Amberlite 400 on a glasswool support. The exchangers were converted into the desired anionic forms and then washed with deionised water till the washings were free of anions taken. The column now stood ready for use.

(i) Separation of Cu(II) based on the precipitate of sulphide in acidic media

The anion-exchanger in column No. 1 was converted into sulphide form. A solution of known concentration of copper nitrate and other metal ions was passed through the column at the rate of 1 ml/minute^{-1} in acidic medium. Cu(II) was retained by the column in the form of CuS. The rest of the metal ions other than Bi(III), Cd(II), Pb(II), As(III), Sb(III), Hg(II) passed out unabsorbed as eluate I. Resin having CuS precipitate was repeatedly treated with 4 M nitric acid at 50°C. The eluate consisting of copper nitrate was collected.

(ii) Separations of Fe(III), Al(III) and Cr(III) based on the precipitate of hydroxides

The eluate I was boiled off to remove H_2S gas. The anion-exchanger in column no. 2 was converted into hydroxide form by the treatment of ammonium hydroxide. 2 ml solution of ammonium chloride was also poured into the column prior to the addition of eluate I at the rate of 1 ml minute^{-1}. Fe(III), Al(III) and Cr(III) were retained over the column in the form of $Fe(OH)_3$, $Al(OH)_3$ and $Cr(OH)_3$ as precipitates. The other metal ions which remained unabsorbed were collected as eluate II. The precipitate was washed with hot deionized water. The dissolution of the precipitate in the resin matrix was then effected by addition of

a dilute solution of hydrochloric acid. The anion-exchanger in column No. 3 was converted into hydroxide form by the treatment of 0.5 M sodium hydroxide. The above filtrate was passed over the column whereby Fe(III) and Cr(III) were retained as ferric hydroxide and chromium hydroxide while aluminium(III) passed out unabsorbed as $NaAlO_2$.

The column having the precipitates was treated with hot sodium hydroxide and excess of bromine water (60°C). This resulted in the detachment of Cr(III) from the resin leaving $Fe(OH)_3$ in the column. Iron precipitate was then dissolved in 4 M hydrochloric acid and eluted iron(III) was collected in a beaker.

(iii) Separations of Ni(II), Mn(II), Zn(II) and Co(II) based on the precipitate of sulphide in alkaline medium

The anion-exchanger in column no. 4 was converted into sulphide form. 5 gm ammonium chloride and 5 ml of ammonia solution (B.D.H.) were added in the eluate II. Then the solution was passed over the column number 4 at the rate of 1 ml $minute^{-1}$. Ni(II), Zn(II), Mn(II) and Co(II) were retained over the column as sulphides while the other cations passed out unretained and were collected as eluate III.

The precipitate was washed with hot deionised water. The column was then treated with 1 N hydrochloric acid. Zn(II) and Mn(II) passed out unabsorbed and collected as F_1. A complete

washing of the column was done to remove Zn(II) and Mn(II) while Ni(II) and Co(II) were retained in the column. The column was then treated with 6M HCl + 6M HNO_3 (3:1) and the filtrate containing Ni(II) and Co(II) was collected as F_2.

The filtrate F_1 was boiled off to remove H_2S gas which was tested by a paper of lead acetate. The anion-exchanger in column no. 5 was treated with excess of 0.5M sodium hydroxide solution. Repeated washings were made with deionized water. Filtrate F_1 was passed over the column at the rate of 1 ml $minute^{-1}$. Mn(II) was retained by the column while Zn(II) passed out unabsorbed as $NaZnO_2$. The precipitate $Mn(OH)_2$ was treated with nitric acid and the effluent was collected in a separate beaker.

Column no. 6 having anion-exchanger in chloride form was converted into hydroxide form by passing 1M ammonium hydroxide solution and then washing the column with deionized water. 5 ml of dimethylglyoxime was added in the column. Nickel(II) was retained over the column in the form of red precipitate of nickel dimethylglyoxime while cobalt(II) solution passed out unabsorbed. The column having nickel(II) precipitate was treated with 4N hydrochloric acid. The effluent was collected which contained nickel(II) ions only.

(iv) Separation of Ba(II) and Sr(II) based on the precipitate of carbonate

To eluate III was added 4 N hydrochloric acid to make it sufficiently acidic and then was boiled off to remove H_2S gas. NH_4OH was added to the above eluate making it basic and was marked as eluate IIIA. The anion-exchanger in column no. 7 was treated with excess of 1 M ammonium carbonate to covert it into carbonate form. 2 ml of NH_4OH was poured into the column. Warm eluate IIIA was added in the aforesaid column. Ba(II) and Sr(II) formed precipitate as $Ba(CO_3)_2$ and $Sr(CO_3)_2$ and were retained over the column while Mg(II) was collected as an eluate IV.

The precipitate in the column was repeatedly washed by deionized water. Dilute acetic acid was then trickled through the column. Ba(II) and Sr(II) precipitates got dissolved and collected as eluate V.

The above column was thoroughly washed with deionised water to remove acetic acid. The anion-exchanger in the above column was converted into chromate form. The eluate V was added to the column. Ba(II) was retained over the column as barium chromate while Sr(II) was collected as an eluate VA. The precipitate of $BaCrO_4$ was dissolved by the treatment of 0.1 M hydrochloric acid. The collected effluent contained only Ba(II) ions.

Eluate IV contained magnesium ions in the form of magnesium carbonate.

Separation of calcium and magnesium as major constituents in dolomite sample

2 gm of ground sample was weighed accurately into a platinum dish. 100 ml of water, 10 ml of perchloric acid and 25-30 ml of hydrofluoric acid were added. The mixture was swirled to achieve thorough mixing. It was partially covered with a lid and then evaporated to dense fumes of perchloric acid. The dish was allowed to cool down. Its sides and the lid were rinsed with deionized water. The dish was again heated to dryness. To the residue in the dish was added 1 ml of hydrochloric acid and 10 ml of deionized water. It was warmed a little to dissolve the content and then cooled. The lid and dish were scrubbed with a rubber policeman and the content was transferred to a 250 ml volumetric flask. It was finally diluted to the mark with deionized water and was thoroughly mixed. Calcium oxide and (calcium oxide + magnesium oxide) were determined by EDTA titration. For magnesium oxide the second reading was substracted from the first reading.

An anion-exchanger in column was treated with excess of $(NH_4)_2CO_3$ to convert it into carbonate form. 2 ml of NH_4OH was also poured into the column. The above stock solution of

dolomite sample was added to the column. Magnesium was collected as an effluent while calcium was retained in the form of calcium carbonate. Into this column, dilute acetic acid was added and the fractions of calcium were collected in a separate beaker. The determination of calcium oxide and magnesium oxide was made by EDTA titration.

RESULTS

The results of some synthetic mixtures are presented in Table 23 and that of a rock samples in Table 24. The results of rock samples are compared with those already known as standards.

TABLE 23

ANALYTICAL DATAS FOR THE SEPARATION OF SYNTHETIC STANDARDS

SL. NO.	SPECIES	TAKEN ppm.	FOUND ppm.
1.	Cu(II)	200	180
2.	Cr(III)	48	42
3.	Al(III)	48	46
4.	Fe(III)	85	80.5
5.	Mn(II)	95	94.5
6.	Zn(II)	180	175
7.	Ni(II)	500	440

TABLE 24

ANALYSIS OF STANDARD ROCK SAMPLES

SAMPLE	TRACE ELEMENTS	VALUES BEFORE SEPARATION	VALUES AFTER SEPARATION
G-2	Mn(II)	220	200
	Zn(II)	54	44
	Ba(II)	1870	1560
W-1	Zn(II)	86	84.5
	Ni(II)	76	70.5
	Cu(II)	110	100
	Ba(II)	160	150
	Sr(II)	190	183
Poc-1	Cr(III)	1800	1600
	Ni(II)	285	185
	Mn(II)	700	650

The results of major constituents determined in the dolomite sample are given below:

Before Separation

(i)	The reading of calcium oxide	= 5.5 ml
(ii)	The reading of calcium oxide and magnesium oxide	= 10.2 ml
	The reading of magnesium oxide	= 4.7 ml

(a) The percentage of calcium oxide in the sample

= 0.5608 x A x 10

Here A = reading of calcium ion

Page = 0.5608 x 10 x 5.5

= 55 x 0.5608

= 30.844

Percentage of calcium oxide in the sample = 30.84

(b) The percentage of magnesium oxide in the sample

= 0.4032 x A x 10

= 0.4032 x 4.7 x 10

= 0.4032 x 47

= 18.9504

Page of magnesium in the sample = 18.9504

After Separation

(i) The reading of calcium oxide = 5.4 ml

(ii) The reading of magnesium oxide = 4.8 ml

(a) The percentage of calcium oxide in dolomite sample

= 0.5608 x A x 10

= 0.5608 x 10 x 5.4

= 0.5608 x 54

= 30.2832

%age of calcium oxide in the sample = 30.28

(b) Percentage of magnesium oxide in dolomite sample

= 0.4032 x 10 x A

= 0.4032 x 10 x 4.8

= 0.4032 x 48

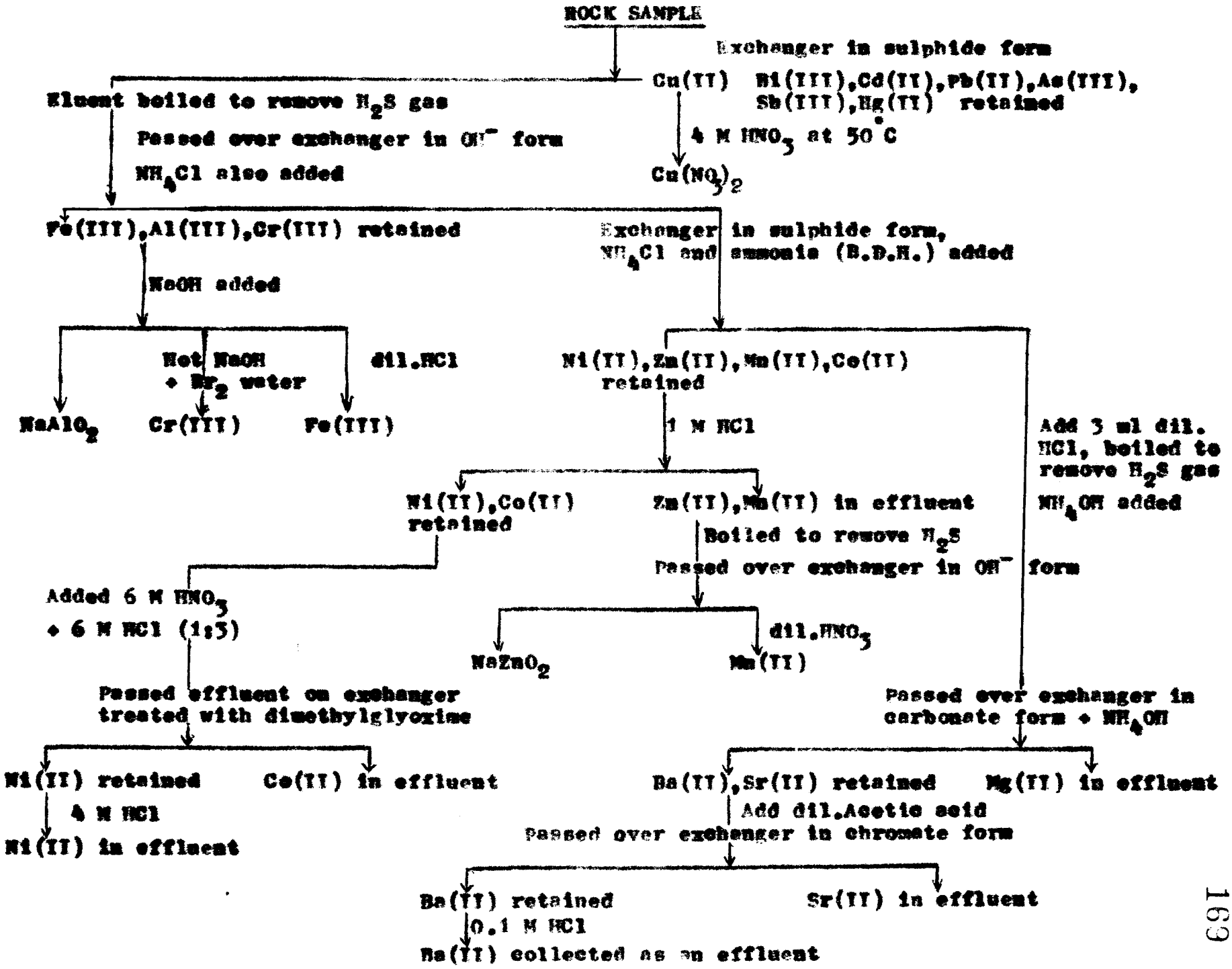
= 19.3536

%age of magnesium oxide in the dolomite sample = 19.35

DISCUSSION

The results of Tables 23 and 24 reveal the use of ion-exchange resins as a means for prior separation to atomic absorption determinations. The results of the determination of 9 metal ions as trace elements when compared with standard results show resemblances. The technique used is based on simple principle of solubility product and preferential retention of the metal ions in traces (or in very dilute solutions) by ion-exchange columns. This method opens a chance for other separations to be tried in this manner. The separation scheme given on the next page gives the view of the application procedure of the method.

This technique is equally useful for the determination of major constituents in rock samples and the usual interferences caused by the other metal ions in the determination of calcium and magnesium ions are got rid of by the use of ion-exchange procedure.


ROCK SAMPLE
Exchanger in sulphide form
Cu(II)
Bi(III),Cd(II),Pb(II),As(III),
Sb(III),Hg(II) retained
4 M HNO3 at 50°C
Cu(NO3)2
Eluent boiled to remove H2S gas
Passed over exchanger in OH⁻ form
NH4Cl also added
Fe(III),Al(III),Cr(III) retained
Exchanger in sulphide form,
NH4Cl and ammonia (B.D.H.) added
NaOH added
Hot NaOH
+ Br2 water
dil.HCl
NaAlO2
Cr(III)
Fe(III)
Ni(II),Zn(II),Mn(II),Co(II)
retained
1 M HCl
Add 3 ml dil.
HCl, boiled to
remove H2S gas
NH4OH added
Ni(II),Co(II)
retained
Zn(II),Mn(II) in effluent
Boiled to remove H2S
Passed over exchanger in OH⁻ form
Added 6 M HNO3
+ 6 M HCl (1:5)
NaZnO2
dil.HNO3
Mn(II)
Passed effluent on exchanger
treated with dimethylglyoxime
Passed over exchanger in
carbonate form + NH4OH
Ni(II) retained
Co(II) in effluent
4 M HCl
Ni(II) in effluent
Ba(II),Sr(II) retained
Mg(II) in effluent
Add dil.Acetic acid
Passed over exchanger in chromate form
Ba(II) retained
Sr(II) in effluent
0.1 M HCl
Ba(II) collected as an effluent

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ZINC SILICATE AS A NEW ADSORBENT FOR PAPER CHROMATOGRAPHIC SEPARATION OF PHENOLS

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ABSTRACT

A new adsorbent zinc silicate has been used for the paper chromatographic separations of different phenols. R_F values have been determined and compared with those obtained on plain papers. A new term R_i has been calculated for various phenols. The dependance of R_i and R_F on various factors have also been studied and discussed.

INTRODUCTION

Efforts have been made to find a suitable adsorbent for the separation of different phenols by many workers recently (1,2). Many authors have studied the chromatography of phenols on plain papers (3-6). Clark suggested use of ion exchange papers for the separation of phenols (7). Most of the sorbents used earlier either interfered with the detection of phenols applied or lacked adequate resolution of different components present in a mixture. Stannic molybdate (8) an inorganic ion

exchanger has been employed as adsorbent for paper chromatography of some phenols. Though they are good for separation purposes the invariable elongation of spots have been a negative point. In our present studies we have used zinc silicate as a potential adsorbent for the phenols.

The spots obtained are compact and distinct.

MATERIALS AND METHODS

Apparatus. Chromatography was achieved on Whatmann No. 3 paper strips of 14 x 3 cms. using glass jars measuring 20 x 5 cms.

Reagents. Chemicals and solvents were of E.Merch (Dermstadt) and B.D.H. analar grade. Zinc nitrate and sodium silicate (Riedel) were used.

Developer. Ammonium hydroxide of different concentration was used.

Detector. One part of mercury was dissolved in one part of fuming nitric acid and diluted with two parts of water. This reagent was used as detector. Ferric nitrate solution was also used for the detection of some phenols.

Preparation of ion exchange papers. Aqueous solutions of zinc nitrate (0.25M) and sodium silicate were prepared. Paper strips of required size (11 cms x 3) were first dipped in zinc nitrate solution for 3-5 seconds. The excess of the reagent was removed by placing the strips over ordinary filter sheet and allowing them to dry for 15 minutes at room

temperat. The strips were then dipped in sc
silicate solution for about 5 secon e excess of
llowed to drain off strips
were placed over a filter sheet. Thes
dried at room temperature and then was
distilled water to remove the excess c
Finally these were dried at room tempe
as such for chromatography.

Procedure. One or two spots of test solutions were placed on the paper strips with the help of thin glass capillaries. The paper was conditioned for about 15 minutes and the solvent was then allowed to ascend (11 cms. in every case).

RESULTS

A small drop of phenol solution was placed on a paper impregnated with zinc silicate. The chromatography of 27 phenols was achieved in ammonia solutions (1×10^{-2}M, 1×10^{-1}M, 5×10^{-1}M, 1M) on zinc silicate papers. The results are summarized in Table 1.

For comparison phenols were chromatographed on untreated Whatmann No. 3 papers in the aforesaid solvent systems (Table 2). Thus a new term R_i (9) was calculated by substracting R_F value for untreated Whatmann No. 3 from R_F value for treated papers (Table 3).

Separation. Separations were tried for the phenols having appreciable difference in their R_F values. Spots of the mixtures were placed on the chromato-

TABLE 1

R_F Values of 27 Phenols in Different Solutions of Ammonia

Sl. No.	Phenols	1 x 10^{-2}M NH_4OH	1 x 10^{-1}M NH_4OH	5 x 10^{-1}M NH_4OH	1M NH_4OH
1.	Phloroglucinol	0.43	0.52	0.60	0.62
2.	α-Naphthol	0.34	0.40	0.42	0.45
3.	β-Naphthol	0.22	0.35	0.40	0.47
4.	2,4 Dinitrophenol	0.32	0.40	0.42	0.45
5.	p-Nitrophenol	0.49	0.50	0.56	0.59
6.	Catechol	0.62	0.66	0.70	0.75
7.	m-Cresol	0.00	0.00	0.00	0.00
8.	p-Cresol	0.00	0.00	0,00	0.00
9.	Phenol	0.00	0.00	0.00	0.00
10.	Resorcinol	0.42	0.51	0.54	0.60
11.	Gallic acid	0.10	0.20	0.27	0.32
12.	o-Nitrophenol	[illegible]	0.08	0.07	0.08
13.	m-Nitrophenol	0.45	0.50	0.54	0.57
[illegible]	Xylenol	0.59	0.67	0.70	0.72
[illegible]	[illegible]nhydrone	0.45	0.60	0.65	0.70
[illegible]	[illegible]nol	0.51	0.60	0.64	0.70
17.	Picric acid	0.65	0.68	0.71	0.74
18.	Vanilline	0.54	0.58	0.59	0.61
19.	Pyrogallol	0.28	0.34	0.42	0.51
20.	Bromothymol blue	0.63	0.68	0.69	0.73
21.	Di(2 hydroxyphenylimino) ethane	0.00	0.02	0.05	0.09
22.	8-Hydroxy 7 iodoquinoline 5 sulfonic acid	0.68	0.70	0.73	0.76
[illegible]	Phenyl fluorone (9,phenyl 2,3,7 trihydroxy 6 fluorone)	0.00	0.00	0.01	0.03
[illegible]	Chlorophenol	0.00	0.00	0.00	0.00
[illegible]	Bromoc[illegible]en	0.66	0.72	0.74	0.81
[illegible]	[illegible]henol[illegible]	0.41	0.56	0.60	0.65
[illegible]	[illegible]	[illegible]	0.63	0.66	0.70

TABLE 3

R_f Values of 26 Phenols

Sl. No.	Phenols	R_f Values			
		1×10^{-2}M NH_4OH	1×10^{-1}M NH_4OH	5×10^{-1}M NH_4OH	1M NH_4OH
1.	Phloroglucinol	0.22	0.22	0.21	0.23
2.	α-Naphthol	0.07	0.14	0.15	0.15
3.	β-Naphthol	0.10	0.11	0.10	0.10
4.	2,4 Dinitrophenol	0.08	0.08	0.10	0.11
5.	p-Nitrophenol	0.06	0.10	0.06	0.06
6.	m-Cresol	0.00	0.00	0.00	0.00
7.	Catechol	0.20	0.21	0.21	0.20
8.	p-Cresol	0.00	0.00	0.00	0.00
9.	Phenol	0.00	0.02	0.02	0.04
10.	Resorcinol	0.20	0.19	0.20	0.20
11.	Gallic acid	0.46	0.37	0.31	0.33
12.	o-Nitrophenol	0.00	0.00	0.01	0.00
13.	m-Nitrophenol	0.11	0.09	0.09	0.11
14.	Xylenol	0.21	0.20	0.21	0.23
15.	Quinhydrone	0.15	0.18	0.23	0.21
16.	Quinol	0.21	0.20	0.17	0.20
17.	Picric acid	0.10	0.12	0.09	0.10
18.	Vanilline	0.09	0.10	0.11	0.10
19.	Pyrogallol	0.32	0.25	0.25	0.23
20.	Bromothymol blue	0.07	0.09	0.11	0.10
21.	Di (2 hydroxyphenylimino) ethane	0.00	0.02	0.02	0.02
22.	Quinoline 5 sulfonic acid	0.06	0.10	0.09	0.08
23.	Phenyl fluorone (9 Phenyl 2,3,7 trihydroxy 6 fluorone)	0.00	0.00	0.01	0.00
24.	4 Chlorophenol	0.00	0.00	0.00	0.00
25.	Bromocresol green	0.14	0.16	0.12	0.13
26.	Aminophenol	0.13	0.10	0.13	0.12

TABLE 4

Separations Achieved on Impregnated Zinc Silicate Papers

Sl. No.	Separation		Solvent
	Of R_F	From R_F	
	Binary Separations		
1.	Phloroglucinol (0.60)	Phenol (0.00)	1M
2.	Phloroglucinol (0.60)	m-Cresol (0.00)	"
3.	Phloroglucinol (0.60)	p-Cresol (0.00)	"
4.	Di (2 hydroxyphenylimino) ethane (0.08)	Phloroglucinol (0.61)	"
5.	Phenyl fluorone (0.00)	Phloroglucinol (0.61)	"
6.	4-Chlorophenol (0.00)	Phloroglucinol (0.60)	"
7.	p-Nitrophenol (0.58)	m-Cresol (0.00)	"
8.	p-Nitrophenol (0.59)	p-Cresol (0.00)	"
9.	p-Nitrophenol (0.59)	Phenol (0.00)	"
10.	Di(2 hydroxyphenylimino) ethane (0.08)	p-Nitrophenol (0.59)	"
11.	4-Chlorophenol (0.00)	p-Nitrophenol (0.58)	"
12.	Phenylfluorone (0.05)	p-Nitrophenol (0.58)	"
13.	m-Nitrophenol (0.55)	m-Cresol (0.00)	"
14.	m-Nitrophenol (0.55)	p-Cresol (0.00)	"
15.	m-Nitrophenol (0.55)	Phenol (0.00)	"
16.	Di(2 hydroxyphenylimino) ethane (0.08)	m-Nitrophenol (0.55)	"
17.	4-Chlorophenol (0.00)	m-Nitrophenol (0.55)	"
18.	Phenylfluorone (0.05)	m-Nitrophenol (0.55)	1M
19.	Catechol (0.70)	Phenol (0.00)	"
20.	Catechol (0.70)	m-Cresol (0.00)	"
21.	Catechol (0.70)	p-Cresol (0.00)	"
22.	4-Chlorophenol (0.00)	Catechol (0.70)	"
23.	Di(2 hydroxyphenylimino) ethane (0.08)	Catechol (0.70)	"
24.	Phenylfluorone (0.05)	Catechol (0.70)	"
25.	Resorcinol (0.60)	Phenol (0.00)	"
26.	Resorcinol (0.60)	m-Cresol (0.00)	"
27.	Resorcinol (0.59)	p-Cresol (0.00)	"
28.	Di(2 hydroxyphenylimino) ethane (0.08)	Resorcinol (0.60)	"
29.	Phenylfluorone (0.05)	Resorcinol (0.58)	"
30.	4- [illegible] enol (0.00)	Resorcinol (0.58)	"
31.	X[illegible] (0.70)	Phenol (0.00)	"
32.	Xylenol (0.70)	m-Cresol (0.00)	"
33.	Xylenol (0.69)	p-Cresol (0.00)	"
34.	Xylenol (0.70)	Phenylfluorone (0.05)	"
35.	Di(2 hydroxyphenylimino) ethane (0.08)	Xylenol (0.70)	
36.	4-Chlorophenol (0.00)	Xylenol (0.70)	"
37.	Quinhydrone (0.68)	m-Cresol (0.00)	"
38.	Quinhydrone (0.68)	p-Cresol (0.00)	"
39.	Quinhydrone (0.68)	[illegible] (0.00)	
40.	[illegible] (0.00)	[illegible] drone (0.68)	
	[illegible] ethane (0.08)	Quinhydrone (0.68)	
41.	[illegible] Fluorone (0.05)	Quinhydrone (0.68)	"
42.	Quinol (0.70)	m-Cresol (0.00)	
		[illegible] (0.00)	

TABLE 4 (Continued)

Sl. No.	Separation Of R_F		Separation From R_F	Solvent
45.	Quinol (0.70)		Phenol (0.00)	"
46.	Di(2 hydroxyphenylimino)	ethane (0.08)	Quinol (0.70)	"
47.	4-Chlorophenol (0.00)		Quinol (0.70)	"
48.	Phenylfluorone (0.05)		Quinol (0.68)	"
49.	Picric acid (0.73)		m-Cresol (0.00)	"
50.	Picric acid (0.73)		p-Cresol (0.00)	"
51.	Picric acid (0.72)		Phenol (0.00)	"
52.	o-Nitrophenol (0.07)		Picric acid (0.72)	"
53.	Quinol (0.71)		o-Nitrophenol (0.07)	"
54.	o-Nitrophenol (0.06)		m-Nitrophenol (0.23)	"
55.	p-Nitrophenol (0.57)		o-Nitrophenol (0.06)	"
56.	o-Nitrophenol (0.07)		Phloroglucinol (0.04)	"
57.	Catechol (0.71)		o-Nitrophenol (0.07)	"
58.	Resorcinol (0.58)		o-Nitrophenol (0.07)	"
59.	Di(2 hydroxyphenylimino)	ethane (0.08)	Picric acid (0.73)	"
60.	Phenylfluorone (0.05)		Picric acid (0.72)	1M
61.	4-Chlorophenol (0.00)		Picric acid (0.72)	"
62.	Vanilline (0.60)		m-Cresol (0.00)	"
63.	Vanilline (0.60)		Phenol (0.00)	"
64.	Vanilline (0.60)		p-Cresol (0.00)	"
65.	Vanilline (0.60)		o-Nitrophenol (0.07)	"
66.	Phenylfluorone (0.05)		Vanilline (0.60)	"
67.	Di(2 hydroxyphenylimino)	ethane (0.07)	Vanilline (0.60)	"

68.	4-Chlorophenol (0.00)		Vanilline (0.60)	"
69.	Bromothymol blue (0.72)		Phenol (0.00)	"
70.	Bromothymol blue (0.72)		p-Cresol (0.00)	"
71.	Bromothymol blue (0.72)		m-Cresol (0.00)	"
72.	Bromothymol blue (0.73)		o-Nitrophenol (0.07)	"
73.	4-Chlorophenol (0.00)		Bromothymol blue (0.72)	"
74.	Di(2 hydroxyphenylimino)	ethane (0.08)	Bromothymol blue (0.72)	"
75.	Phenylfluorone (0.05)		Bromothymol blue (0.72)	"
76.	Bromocresol green (0.80)		Phenol (0.00)	"
77.	Bromocresol green (0.80)		p-Cresol (0.00)	"
78.	Bromocresol green (0.79)		m-Cresol (0.00)	"
79.	Bromocresol green (0.80)		o-Nitrophenol (0.07)	"
80.	Di(2 hydroxyphenylimino)	ethane (0.07)	Bromocresol green (0.79)	"
81.	4-Chlorophenol (0.00)		Bromocresol green (0.80)	1M
82.	Phenylfluorone (0.05)		Bromocresol green (0.80)	"
83.	Phenolphthalein (0.65)		Phenol (0.00)	"
84.	Phenolphthalein (0.65)		p-Cresol (0.00)	"
85.	Phenolphthalein (0.66)		m-Cresol (0.00)	"
86.	Phenolphthalein (0.66)		o-Nitrophenol (0.07)	"
87.	4-Chlorophenol (0.00)		Phenolphthalein (0.65)	"
88.	o-Aminophenol (0.70)		Phenol (0.00)	"
[illegible]	[illegible]phenol (0.70)		p-Cresol (0.00)	"
[illegible]	[illegible]nol (0.70)		m-Cresol (0.00)	"
	[illegible]	.80)	o-Aminophenol (0.70)	"
	[illegible]	5)	o-Aminophenol (0.71)	"
	[illegible]	1)	[illegible]	"
			[illegible] (0.65)	0.01M
			Bromothymol blue (0.63)	"

TABLE 4 (Continued)

Sl. No.	Separation		Solvent
	Of R_F	From R_F	
	Ternary Separations		
96.	m-Cresol (0.00)	∝-Naphthol (0.45)	Xylenol (0.75)	1M
97.	p-Cresol (0.00)	∝-Naphthol (0.45)	Xylenol (0.75)	"
98.	Phenol (0.00)	∝-Naphthol (0.46)	Picric acid (0.75)	"
99.	4-Chlorophenol (0.00)	∝-Naphthol (0.44)	Picric acid (0.73)	"

graphic papers and developed with the desired developer. Those practically achieved are reported in Table 4.

DISCUSSION

The results presented in Table 1 show R_F values of 27 phenols on papers impregnated with zinc silicate. The spots obtained on these papers are compact and discernible while those found on untreated show considerable trailing. Comparison of the results shown in Tables 1 and 2 revealed that R_F values on treated papers in most of the cases are lower than that obtained on untreated papers. This shows that zinc silicate serves as a good adsorbent for phenols and its immobilization on the paper retards the movement of various phenols to different extent. On plain papers , however, there is no such retardation force and hence a high R_F value is observed on these papers.

Besides the adsorptivity R_F values also depend on the kind of developer used. In the present studies NH_4OH in different concentrations has been used as a developer. The results show that increase in concentration of NH_4OH causes increase in R_F values. Plots of R_F values vs. concentration of ammonia are straight lines with positive papers (Figs.1a-f). This behaviour can be attributed to the high solubility of phenols in higher concentrations of ammonium hydroxide. For the similar reasons R_F values remained extremely low when H_2O was used as a developer.

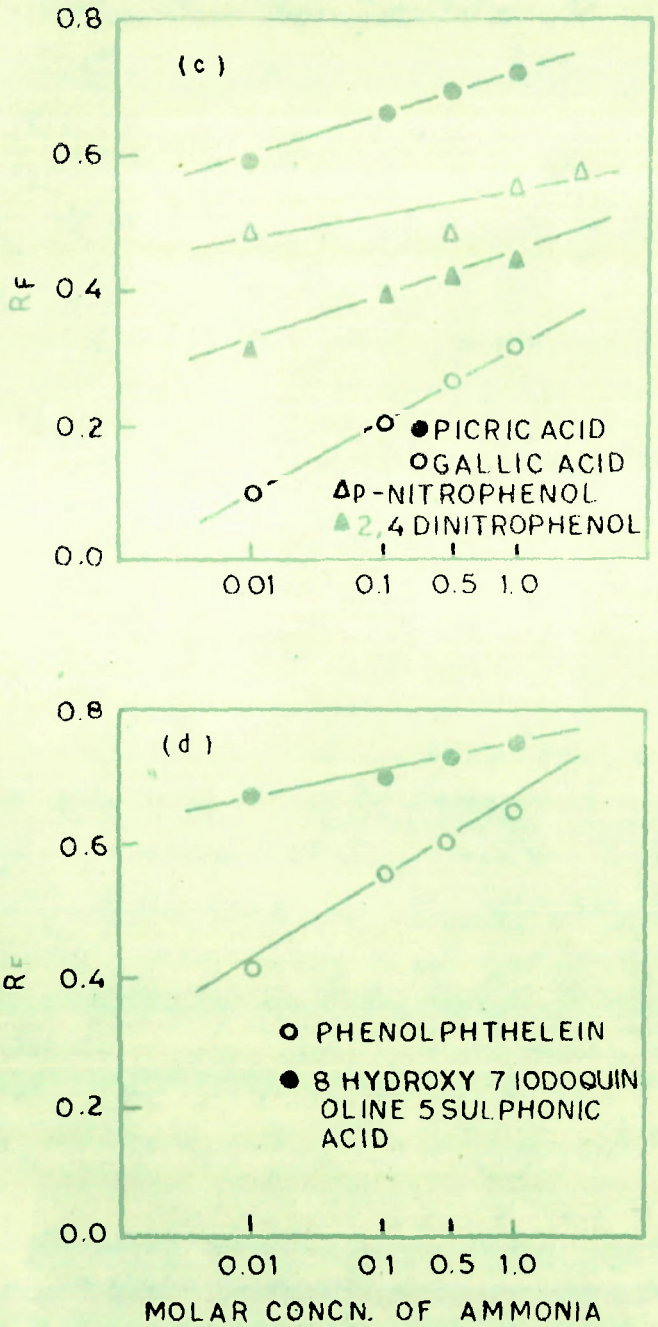

FIGURE 1(c-d) **Plot of R_F against molar concentration of ammonia.**

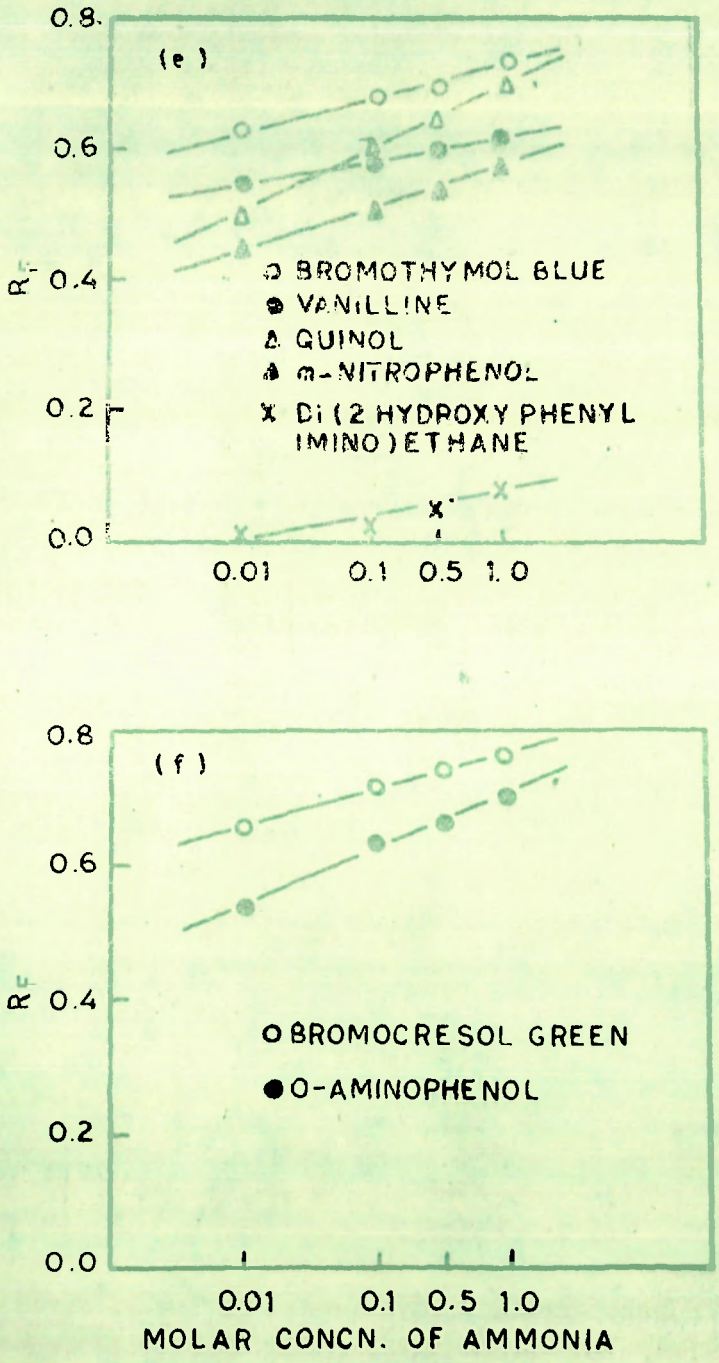

FIGURE 1(e-f) Plot of R_F against molar concentration of ammonia.

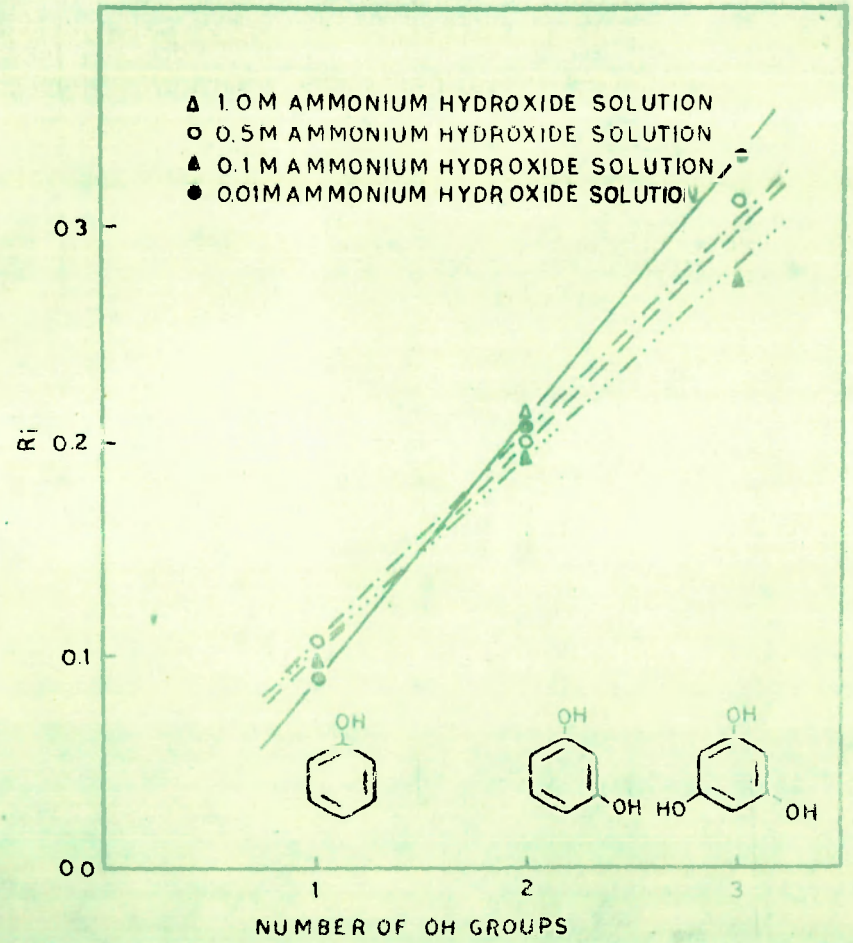

FIGURE 2 Plot of R_f against number of -OH groups.

R_f values R_{m_1}-R_{m_2} have been determined for various phenols which is a measure of ion exchange effect (Table 3). The results of this table indicate that for a particular phenol R_f remains constant for the different concentrations of NH_4OH, while R_f values are found to depend on the number of -OH groups present in phenol (Fig. 2). R_f of the phenol having three

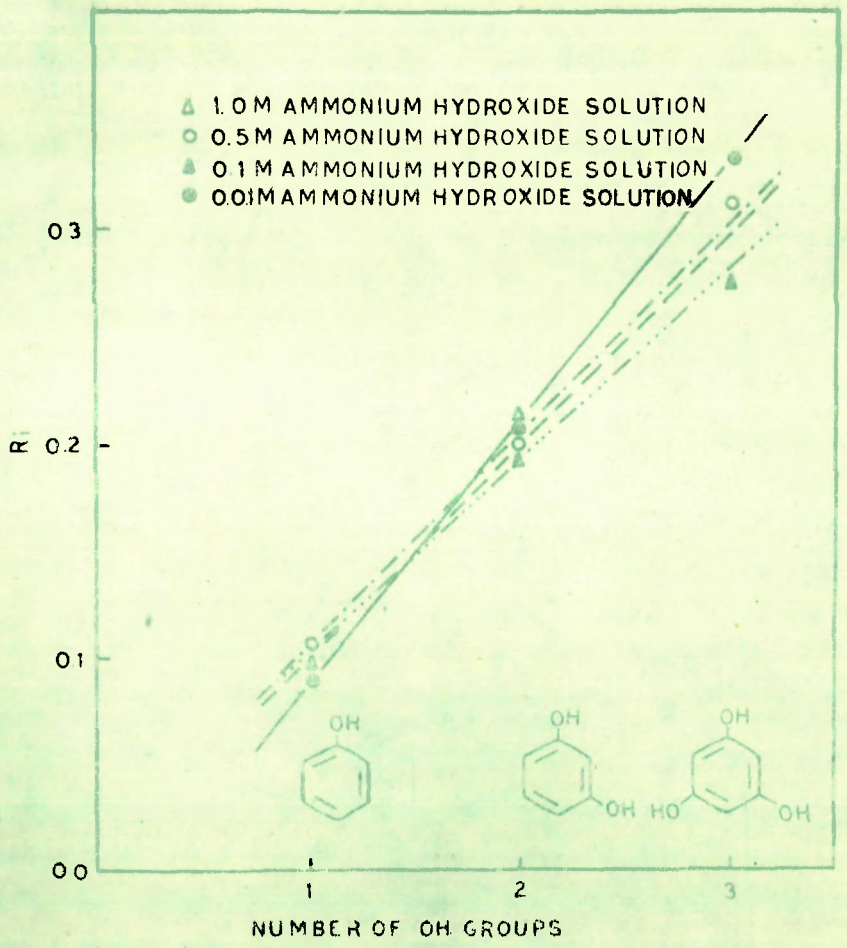

FIGURE 2 Plot of R_i against number of -OH groups.

R_i values $R_{...}$-$R_{...}$ have been determined for various phenols which is a measure of ion exchange effect (Table 3). The results of this table indicate that for a particular phenol R_i remains constant for the different concentrations of NH_4OH while R_i values are found to depend on the number of -OH groups present in phenol (Fig. 2). R_i of the phenol having three

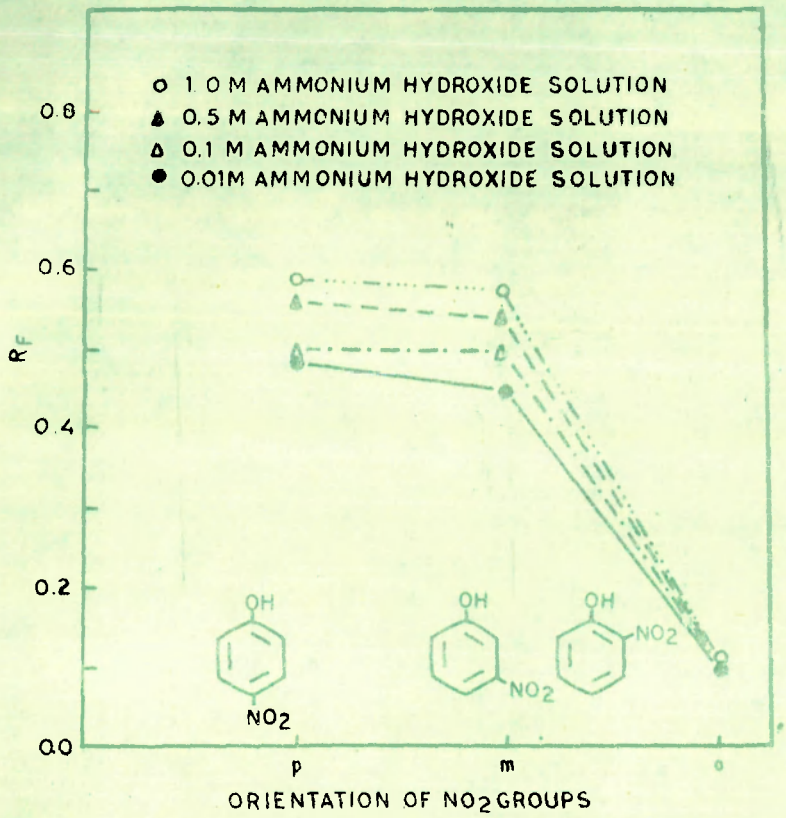

FIGURE 3 Plot of R_F against orientation of -OH groups.

-OH groups is greater than the phenol with two -OH groups which in turn is greater than the one with one -OH group. Since zinc silicate acts as an extremely weak cation exchanger its affinity should be greater for the phenol which can furnish greater number of H^+ ions. This possibility explains why pyrogallol is more strongly adsorbed than catechol and phenol.

The results plotted in Fig. 3 show the dependence of R_F values on the orientation of $-NO_2$

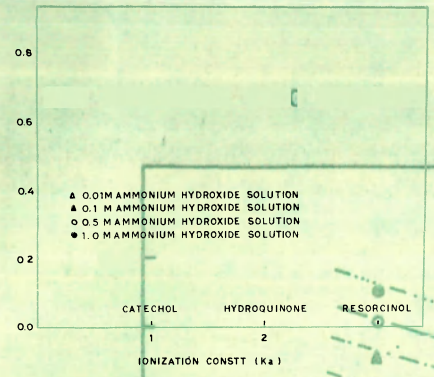

FIGURE 4 Plot of R_F against ionization constant.

groups. The behaviour of orthonitrophenol is different from that of para and metaphenols. The difference in behaviour can be attributed to the possibility of intramolecular hydrogen bonding in o-Nitrophenol which is not found in either para or meta nitrophenol. R_F values have also been found to depend upon the ionization constant of phenol. The plot of R_F vs. ionization constant (Fig. 4) shows that R_F values increase with increasing ionization constant.

Table 4 shows various separation that have been achieved on papers impregnated with zinc silicate.

Separation of o-Nitrophenol from meta and para substituted nitrophenols can be neatly achieved. Some ternary separations have also been possible on these papers.

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TABLE 2

R_F Values of Ph... on Plain Papers in Ammonia Solut...

Sl. No.	Phenols	1 x 10^{-2}M NH_4OH	1 x 10^{-1}M NH_4OH	5 x 10^{-1}M NH_4OH	1M NH_4OH
1.	Phloroglucinol	0.65	[illegible]	0.81	0.85
2.	-Naphthol	0.41	0.54	0.57	0.60
3.	-Naphthol	0.32	0.46	0.50	0.57
4.	2-4 Dinitrophenol	0.40	0.48	0.52	0.56
5.	p-Nitrophenol	0.55	0.60	0.62	0.65
6.	Catechol	0.82	0.87	0.91	0.95
7.	m-Cresol	0.00	0.00	0.00	0.00
8.	p-Cresol	0.00	0.00	0.00	0.00
9.	Phenol	0.00	0.02	0.02	0.04
10.	Resorcinol	0.62	0.70	0.74	0.80
11.	Gallic acid	0.56	0.57	0.58	0.65
12.	o-Nitrophenol		0.08	0.08	0.08
13.	m-Nitrophenol	[illegible]	0.59	0.63	0.68
		0.80	0.87	0.91	0.95
		0.60	0.78	0.88	0.91
14.	Quinol	0.72	0.80	0.85	0.91
15.	Picric acid	0.75	0.80	0.80	0.84
	Vanilline	0.63	0.68	0.70	0.71
	Pyrogallol	0.60	0.65	0.70	0.79
20.	Bromothymol blue	0.70	0.77	0.80	0.83
21.	Di(2 hydroxyphenylimino) ethane	0.00	0.04	0.07	0.11
22.	Quinoline 5 - sulfonic acid	0.74	0.80	0.82	0.84
23.	Pheuyl fluorone (9 Phenyl 2,3,7 trihydroxy 6 fluorone	0.00	0.00	0.04	0.04
24.	4 Chlorophenol	0.00	0.00	0.00	0.00
25.	Bromocresol green	0.80	0.88	0.88	0.94
26.	o-Aminophenol	0.66	0.72	0.79	[illegible]

TABLE 3

R_f Values of 26 Phenols

Sl. No.	Phenols	R_f Values			
		1×10^{-2}M NH_4OH	1×10^{-1}M NH_4OH	5×10^{-1}M NH_4OH	1M NH_4OH
1.	Phloroglucinol	0.22	0.22	0.21	0.23
2.	α-Naphthol	0.07	0.14	0.15	0.15
3.	β-Naphthol	0.10	0.11	0.10	0.10
4.	2,4 Dinitrophenol	0.08	0.08	0.10	0.11
5.	p-Nitrophenol	0.06	0.10	0.06	0.06
6.	m-Cresol	0.00	0.00	0.00	0.00
7.	Catechol	0.20	0.21	0.21	0.20
8.	p-Cresol	0.00	0.00	0.00	0.00
9.	Phenol	0.00	0.02	0.02	0.04
10.	Resorcinol	0.20	0.19	0.20	0.20
11.	Gallic acid	0.46	0.37	0.31	0.33
12.	o-Nitrophenol	0.00	0.00	0.01	0.00
13.	m-Nitrophenol	0.11	0.09	0.09	0.11
14.	Xylenol	0.21	0.20	0.21	0.23
15.	Quinhydrone	0.15	0.18	0.23	0.21
16.	Quinol	0.21	0.20	0.17	0.20
17.	Picric acid	0.10	0.12	0.09	0.10
18.	[illegible]	0.09	0.10	0.11	0.10
	[illegible]	0.32	0.25	0.25	0.23
	[illegible]ol blue	0.07	0.09	0.11	0.10
	[illegible]roxyphenyl[illegible]no) ethane	0.00	0.02	0.02	0.02
	[illegible] 5 sulfonic acid	0.06	0.10	0.09	0.08
	[illegible]uorone (9 Phenyl 2,3,7 [illegible]-6 fluorone)	0.00	0.00	0.01	0.00
24.	4 Ch[illegible]ol	0.00	0.00	0.00	0.00
25.	[illegible]-Aminophenol	0.14	0.16	0.12	0.13
		0.13	0.10	0.13	0.13